2-Fluoro-2,2-dinitroethyl Chloride.—To a stirred solution of 6.24 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol and 3.95 g (0.04 mol) of pyridine in 50 ml of methylene chloride was added dropwise at 0–5° with cooling 2.7 g (0.02 mol) of sulfuryl chloride. No visible reaction. After 45 min, the reaction mixture was warmed to 25° and was allowed to stand for 7 days. The solution was washed with 200 ml of ice-cold 1% sulfuric acid and distilled to give 3.4 g of 2-fluoro-2,2-dinitroethyl chloride, bp 22–23° (0.2 mm), n^{23}D 1.4270.

Anal. Calcd for $C_2H_2N_2ClFO_4$: C, 13.9; H, 1.2; N, 16.2; F, 11.0. Found: C, 13.8; H, 1.0; N, 15.4; F, 11.1.

Differential thermal analysis showed an endotherm at 156°, the boiling point of the compound.

Proton nmr (CCl_4): δ 4.60 (d, J_{HF} = 16.1 Hz). Fluorine nmr: ϕ 108.2 (s, broad).

Tris(2-fluoro-2,2-dinitroethyl) Borate.—A mixture of 10.8 g (0.07 mol) of 2-fluoro-2,2-dinitroethanol and 2.92 g (0.02 mol) of triethyl borate was heated in a distillation apparatus protected from the atmospheric moisture at 95° for 3 hr, and then ethanol was distilled at reduced pressure. The remaining solid was recrystallized from methylene chloride to give 8.9 g of white crystalline solid which hydrolyzed slowly when exposed to the moist air.

Anal. Calcd for $C_6H_6N_6BF_3O_{15}$: C, 15.3; H, 1.3; N, 17.9; F, 12.1. Found: C, 15.0; H, 1.3; N, 16.9; F, 11.7.

Proton nmr (CH_3CN): δ 4.96 (d, J_{HF} = 16.5 Hz). Fluorine nmr: ϕ 111.9 (t, J_{HF} = 16.2 Hz).

2-Fluoro-2,2-dinitroethyl Nitrate.—To a stirred mixture of 12 ml of 100% nitric acid and 12 ml of concentrated sulfuric acid was added dropwise (5 min) at 0–5° 7.7 g of 2-fluoro-2,2-dinitroethanol. The reaction mixture was stirred for 15 min, added to 100 g of crushed ice, a water-insoluble liquid separated, and washed with 50 m of water, wt 7.5 g (75% yield), bp 62–63° (5 mm), n^{23}D 1.4377 [lit.[4] bp 62–62.5° (5–6 mm), n^{20}D 1.4372].

Registry No.—2-Fluoro-2,2-dinitroethanol, 17003-75-7; allyl 2-fluoro-2,2-dinitroethyl ether, 25171-99-7; 2,2-dinitropropyl methyl ether, 5917-65-7; 2,2-dinitropropyl methyl sulfate, 25172-01-4; 1,3-dimethoxy-2,2-dinitropropane, 25172-02-5; methyl 3-methoxy-2,2-dinitropropyl sulfate, 25172-03-6; 2-fluoro-2,2-dinitroethyl ethyl carbonate, 25172-14-9; 2-fluoro-2,2-dinitroethyl oxalyl chloride, 25172-15-0; 2-fluoro-2,2-dinitroethyl iminodicarboxylate, 25172-16-1; 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 25172-17-2; 2-fluoro-2,2-dinitroethanol *p*-toluenesulfonate, 25172-18-3; 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether, 25172-19-4; 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether *p*-toluenesulfonate, 25172-20-7; 2-fluoro-2,2-dinitroethyl glycidyl ether, 25184-14-9; 4-(2-fluoro-2,2-dinitroethoxy)-3-hydroxybutene 1,2-oxide, 25172-21-8; 2-fluoro-2,2-dinitroethoxyacetic acid, 25172-22-9; 2-fluoro-2,2-dinitroethoxyacetyl chloride, 25172-23-0; 2-fluoro-2,2-dinitroethyoxymethylisocyanate, 25172-24-1; 2-fluoro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethoxyacetate, 25172-25-2; 2,2-dinitropropyl 2-fluoro-2,2-dinitroethoxyacetate, 25172-26-3; bis(2-fluoro-2,2-dinitroethoxyacetate), 25172-27-4; 2-fluoro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethoxymethylcarbamate, 25172-28-5; bis(2-fluoro-2,2-dinitroethoxymethylcarbamate), 25172-29-6; N,N′-bis(2-fluoro-2,2-dinitroethoxymethyl)urea, 25172-30-9, 2-(2-fluoro-2,2-dinitroethoxy)ethyl nitrate, 25172-31-0; 2-fluoro-2,2-dinitroethoxyacetone, 25172-32-1; 2-fluoro-2,2-dinitroethoxyacetone oxime, 25172-33-2; 2,2-dinitropropyl 2-fluoro-2,2-dinitroethyl ether, 25172-34-3; bis(2-fluoro-2,2-dinitroethyl) sulfite, 24590-46-3; 2-fluoro-2,2-dinitroethyl chloride, 25172-36-5; tris(2-fluoro-2,2-dinitroethyl) borate, 25172-37-6.

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Disproportionation of 3,3-Difluorotetrachloropropene. Application of the Hard and Soft Acids and Bases Principle to Organic Halogen Compounds[1]

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Product distributions from the reaction of 3,3-difluorotetrachloropropene (**1a**) at 50° with aluminum chloride and bromide, titanium tetrachloride, and antimony pentachloride were determined. The aluminum and titanium halides were converted to the fluorides by the reaction; the aluminum fluoride so formed was shown to catalyze the disproportionation of **1a**. 1-Bromo-1,2-dichloro-3,3,3-trifluoropropene (**8**) was formed in the reaction with aluminum bromide and was also independently synthesized. Formation of **8** is rationalized in terms of the hard and soft acids and bases (HSAB) concept; numerous examples from the literature are similarly interpreted. The reactions of $AlCl_3$ with 3-fluoropentachloropropene, 3,3,3-trifluorotrichloropropene, and 1,1-difluorotetrachloroethane were also investigated.

The disproportionation of polyhalogenated aliphatic fluorides has long been recognized, and is of commercial significance, particularly in the case of the fluorochloromethanes, as demonstrated by the profusion of patents in this area. It is also well known that aluminum chloride, a catalyst frequently employed in the disproportionation of fluorochloro compounds, is unsuitable for use in Friedel–Crafts alkylations involving aliphatic fluorides, because of its tendency to abstract organically bound fluorine. Information in the literature which contributes to the general understanding of these processes is meager, however, and little, if any, attempt has been made in the past to determine the extent to which the two occur simultaneously.

The question of the relative effectiveness of various Lewis acids in these two reactions also exists. In the disproportionation of 3,3-difluorotetrachloropropene (**1a**), it is reported that catalytic activity decreases in the sequence[3] antimony pentachloride > titanium tetrachloride > aluminum bromide, aluminum chloride > ferric chloride. The order of activity was determined by the length of time required to produce a

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[1] Taken in part from the Ph.D. Thesis of G. C. B., The University of Iowa, Iowa City, Iowa, 1970.

[2] Shell Foundation Fellow, 1965–1966.

[3] M. Prober, *J. Amer. Chem. Soc.*, **76**, 4189 (1954).

TABLE I

REACTION OF PERHALO OLEFINS WITH METAL HALIDES AT 50°

	Reactants					Products				Fluorine balance, mmol
Expt	mmol	Olefin	mmol	Metal halide	Time, hr	TFP, mmol	DFP, mmol	MFP, mmol	HCP, mmol	
1	100	**1a**	10.0	$AlCl_3$	12	48.0	9.4	8.7	33.9	−28.5
2	100	**1a**	10.0	$SbCl_5$	12	8.5	86.7	4.8	0.0	3.7
3[a]	100	**1a**	10.0	$SbCl_5$	36	16.3	70.4	9.0	1.1	1.3
4	100	**1a**	9.8	$TiCl_4$	12	3.0	68.4	12.6	16.0	−41.6
5[b]	100	**1a**	10.0	$AlBr_3$	12	45.2	3.1	4.7	28.5	−28.6[c]
6	105	**1a**	9.9	$FeCl_3$	12	0.0	100.0	0.0	0.0	0.0
7	100	**1a**	10.0	AlF_3	12	0.0	100.0	0.0	0.0	0.0
8[d]	20	**1a**	2.0	BBr_3	12	0.0	19.9+	0.0	0.0	
9[e]	100	**7a**	10.0	$AlCl_3$	12	90.0	4.0	1.0	5.0	−21.0
10	100	**3a**	10.0	$AlCl_3$	12.5	14.8	12.1	16.3	56.8	−14.9[f]

[a] Unknown material eluted after **5a**, ~3.2 mmol. [b] A total of ~17.9 mmol of unknown products was formed. See text. [c] Fluorine content of **8** and **9** included. [d] A trace (0.1 mmol or less) of material was eluted after **1a**. [e] Approximate values; a base-line shift occurred during each analysis of this mixture. [f] Initial fluorine content, 100 mmol.

detectable quantity of the lower boiling 3,3,3-trifluorotrichloropropene (**7**). Formation of this material was indicated by a drop in the reflux temperature at the head of a fractionating column over a flask of the reactants. Stoichiometrically, the disproportionation may be formulated as below.

$$\begin{aligned} &2\mathrm{CCl_2{=}CClCClF_2} \longrightarrow \mathrm{CCl_2{=}CClCF_3} + \mathrm{CCl_2{=}CClCCl_2F} \\ &2\mathrm{CCl_2{=}CClCCl_2F} \longrightarrow \mathrm{CCl_2{=}CClCCl_3} + \mathrm{CCl_2{=}CClCClF_2} \end{aligned} \qquad (1)$$

In the light of other work,[4] the aluminum halides appear too late in the above series of metal halides; further, the method[3] described provides no information about the extent of substitution. Such information would be of interest since, in the case of aluminum halides, substitution would produce aluminum fluoride, which can be a suitable catalyst for both the disproportionation[5] and fluorination[6] of fluorochloroalkanes in the vapor phase. Catalysts of this sort can be prepared by the gas phase reaction of hydrogen fluoride with aluminum chloride,[5] or fluorochloroethanes with alumina at elevated temperatures.[7] The generation *in situ* of catalytically active aluminum fluoride in the reaction of **1a** at reflux temperature or below seems possible. For these reasons a careful reexamination of this reaction was undertaken.

Results and Discussion

When **1a** was prepared by the usual Swarts reaction of hexachloropropene with antimony trifluoride it contained a significant amount (*ca.* 5%) of 2,3,3-trichloroacrylyl fluoride.

It was first thought that **1a** so prepared was contaminated with antimony salts.[8] The recommended treatment with quinoline[8] failed to remove the contaminant, however, as did extraction with ten portions of 1 *N* hydrochloric acid which surely would have removed dissolved antimony salts from such a nonpolar medium.[9] Careful analysis by gas–liquid partition chromatography (glpc) on a silicone rubber column indicated a minor component eluted close to **1a**. The impurity was isolated and characterized as 2,3,3-trichloroacrylyl fluoride; it was conveniently removed from **1a** by treatment with ammonia.

The acid fluoride is believed to have arisen from the reaction of antimony oxide contained in the antimony trifluoride according to reaction 2.

$$\begin{aligned} &3\mathrm{CCl_2{=}CClCCl_3} + \mathrm{Sb_2O_3} \xrightarrow{\mathrm{SbCl_5}} 3\mathrm{CCl_2{=}CClCOCl} + 2\mathrm{SbCl_3} \\ &3\mathrm{CCl_2{=}CClCOCl} + \mathrm{SbF_3} \longrightarrow 3\mathrm{CCl_2{=}CClCOF} + \mathrm{SbCl_3} \end{aligned} \qquad (2)$$

The reaction formulated has a well-known parallel in Knox and Tyree's method of preparation[10] of anhydrous inorganic halides by the reaction of carbon tetrachloride with a metal oxide. Indeed, **5a** has been substituted for carbon tetrachloride in such reactions,[11] although no reaction is reported to occur with antimony pentoxide.[12] It would seem probable that the metal halide would catalyze this exchange by polarization of the carbon–chlorine bond, and perhaps also by formation of an oxychloride soluble in the halide reaction mixture. Similar reactions of organic halides with sulfur oxides in the presence of antimony halides have been reported.[13]

Substitution.—Product distributions in Table I from the various reaction mixtures were obtained by glpc; the organic fluorine balance was calculated from the glpc data as the difference in total organic fluorine content (as mmol F^-) between starting olefin and products, *i.e.*, 3(**7**) + 2(**1a**) + **3a** − initial fluorine content.

Examination of Table I shows that both aluminum chloride and titanium tetrachloride are converted to the corresponding fluorides in reaction with **1a**, whereas antimony pentachloride does not undergo such substitution. In the case of **1a** and aluminum chloride,

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(4) D. J. Burton, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1961.

(5) (a) C. B. Miller, U. S. Patent 2,637,748 (1953); *Chem. Abstr.*, **48**, 2755 (1954). C. B. Miller and J. D. Calfee, U. S. Patent 2,676,996 (1954); *Chem. Abstr.*, **49**, 1770 (1955). (b) H. Agahigian and C. Woolf, German Patent 1,139,831 (1962); *Chem. Abstr.*, **58**, 10075 (1963).

(6) C. Woolf and C. B. Miller, U. S. Patent 2,673,139 (1954); *Chem. Abstr.*, **48**, 10261 (1954). J. D. Calfee and C. B. Miller, U. S. Patent 2,681,267 (1954); *Chem. Abstr.*, **48**, 10958 (1954). C. B. Miller and J. D. Calfee, U. S. Patent 2,748,177 (1956); *Chem. Abstr.*, **51**, 455 (1957).

(7) (a) M. Hauptschein and A. H. Fainberg, U. S. Patent 3,138,559 (1964); *Chem. Abstr.*, **61**, 8188 (1964). (b) British Patent 921,796 (1963); *Chem. Abstr.*, **59**, 9788 (1963).

(8) W. T. Miller, Jr., and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 4164 (1957).

(9) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," Wiley, New York, N. Y., 1957, p 127.

(10) K. Knox, S. Y. Tyree, Jr., R. D. Srivastana, V. Norman, J. Y. Bassett, Jr., and J. H. Holloway, *J. Amer. Chem. Soc.*, **79**, 3358 (1957).

(11) A. B. Bardawil, F. N. Collier, Jr., and S. Y. Tyree, Jr., *J. Less-Common Metals*, **9**, 20 (1965).

(12) W. Porterfield, Ph.D. Thesis, University of North Carolina, Chapel Hill, N. C., 1962.

(13) (a) R. F. Sweeney, B. Veldhuis, E. E. Gilbert, L. G. Anello, R. J. DuBois, and W. J. Cunningham, *J. Org. Chem.*, **31**, 3174 (1966). (b) The reaction of 1,1-dichloroethane with sulfur dioxide in the presence of antimony pentafluoride is mentioned by G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).

precipitation of chloride ion in the aqueous hydrolysate showed substitution to be essentially complete after 1 hr. Thus disproportionation which occurred after that time was almost certainly catalyzed by aluminum fluoride.

These results may be explained in terms of Pearson's concept of hard and soft acids and bases (HSAB).[14] Since aluminum and titanium cations are hard,[14a] they will combine preferentially with hard anions, *i.e.*, fluoride ion. The difference in activity of these two Lewis acids points out the difference between acid *strength* and acid hardness. Although both aluminum chloride and titanium tetrachloride are hard, and both chlorides are apparently *strong* acids since substitution requires carbon–fluorine bond cleavage, there is a marked difference in strength between the resulting aluminum and titanium fluorides. Whereas aluminum fluoride produces considerable disproportionation, as evidenced by the amount of **7** formed, relatively little **7** is produced in the reaction catalyzed by titanium, and the products are predominantly those resulting from substitution, *i.e.*, **3a** and **5a**.

Antimony pentachloride presents a different situation. Apparently it is not a particularly hard acid, since it preferentially combines the softer chloride ion (relative to F^-). This idea is supported by the fluorination of organic chlorine compounds by antimony pentafluoride.[15] Antimony pentachloride produces substantial disproportionation, however, and must therefore be a *strong* Lewis acid. The absence of hexachloropropene in the 12-hr reaction is attributed to consumption of this compound by side reactions with antimony salts. The reaction of water with the solid hexachloropropene–antimony pentachloride complex is reported to lead to hydrolysis of **5a**, whereas hydrolysis of the complex of aluminum chloride with **5a** regenerates hexachloropropene.[16]

The hydrolysis may be envisioned as proceeding by attack of water on the metal to displace chloride ion to yield **5a**, an intermediate metal oxychloride, and hydrogen chloride. In the case of antimony, reaction between hexachloropropene (or the pentachloroallyl cation) and antimony oxychloride (or oxide) would give 2,3,3-trichloroacrylyl chloride in a manner analogous to reaction 2 above.[17]

This reaction may be viewed as a competition between Sb^{5+} and $-C^+Cl_2$ for the hard oxide ion; formation of the acyl halide indicates that $-C^+Cl_2$ is harder. The resemblance to fluorination of the $-CCl_3$ group by antimony trifluoride, in which $-C^+Cl_2$ and Sb^{3+} compete for the hard F^-, may be noted. The unknown material formed in the 36-hr reaction is believed to be octachloropropane formed by the reduction of the antimony to the trichloride. Similar reductions have been previously reported.[11,12]

Since boron halides are usually considered to be hard, reaction of boron tribromide with **1a** might be expected to give boron trifluoride and organic bromide compounds. Essentially no reaction occurs, however, which implies that boron tribromide is a relatively weak Lewis acid; this point is discussed more fully in the following section.

That substitution occurs with aluminum bromide is obvious from the formation of bromopropenes. The amount and order of elution of the unknown products for a typical experiment were 7.8% after **7**, 0.5% after **1a**, 0.4% after **3a**, 9.2% after **5a**. The formation of a bromopropene having a retention time less than **1a** was perplexing, since these materials elute in order of boiling point on a silicone rubber column, and substitution of bromine for either chlorine or fluorine would result in an increased boiling point. Small amounts of the bromopropenes eluted immediately after **7** and **1a** were isolated. The infrared spectrum of each showed the presence of the trifluoromethyl group, as well as unsaturation. The spectra, particularly that of the lower boiling component, were quite similar to the spectrum of **7**, except that the bands were shifted to longer wavelength, which is characteristic of substitution of bromine for chlorine in such systems.[18] The two compounds were thus assigned the structures $CF_3CCl{=}CClBr$ and $CF_3CCl{=}CBr_2$. The infrared spectrum and glpc retention time of 1-bromo-1,2-dichloro-3,3,3-trifluoropropene (**8**), synthesized by an independent route, were identical with that of the unknown eluted between **7** and **1a**. The evidence available does not exclude the possibility that materials isolated from the reaction of aluminum bromide with **1a** may contain bromine in the 2 position; substitution in the 2 position seems unlikely, however.

Disproportionation.—From the preceding discussion and the data in Table I, it is apparent that the order of activity in the disproportionation of **1a** is aluminum chloride, aluminum bromide (aluminum fluoride) > antimony pentachloride > titanium tetrachloride (titanium tetrafluoride) > boron tribromide, ferric chloride, commercial aluminum fluoride (inactive). That the aluminum halides (excluding commercial aluminum fluoride) are clearly more active than the others listed is further shown by the fact that aluminum chloride with 1,1-difluorotetrachloroethane gave both disproportionation and substitution reactions. The rapidity and extent of these reactions were very similar to those of **1a** with aluminum chloride; this result was unexpected since it was thought that resonance stabilization of **2** would make the reaction of **1a** more facile. The difference in reactivity between **1a** and the ethane was obvious in the case of antimony pentachloride and titanium tetrachloride, since 1,1-difluorotetrachloroethane did not undergo reaction in their presence at 50°

The activity sequence above may be viewed as a qualitative scale of Lewis acidity. The positions of aluminum and antimony halides is consistent with the finding[16] that the 1:1 complex of **5a** and aluminum chloride exists as the pentachloroallyl cation (**4**) in methylene chloride solution, whereas with antimony pentachloride **5a** in solution is largely uncomplexed. Further, it is reported[19] that no complex formation

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(14) (a) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963). (b) R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

(15) R. A. Davis, U. S. Patent 3,201,483 (1965); *Chem. Abstr.*, **63**, 13074 (1965).

(16) R. West and P. T. Kwitowski, *J. Amer. Chem. Soc.*, **88**, 5280 (1966).

(17) (a) The hydrolysis of 2-fluorotrichlorocyclopropene to 2,3-dichloroacrylyl fluoride with antimony pentachloride and moisture is reported in ref (18b). (b) The presence of benzoyl chloride in the product mixture from the reaction of $C_6H_5CF_2Cl$ with antimony pentachloride followed by hydrolysis is mentioned in ref 1.

(18) (a) R. West and P. T. Kwitowski, *J. Amer. Chem. Soc.*, **90**, 4697 (1968); (b) S. W. Tobey and R. West, *ibid.*, **88**, 2481 (1966).

(19) R. West, A. Sado, and S. W. Tobey, *ibid.*, **88**, 2488 (1966).

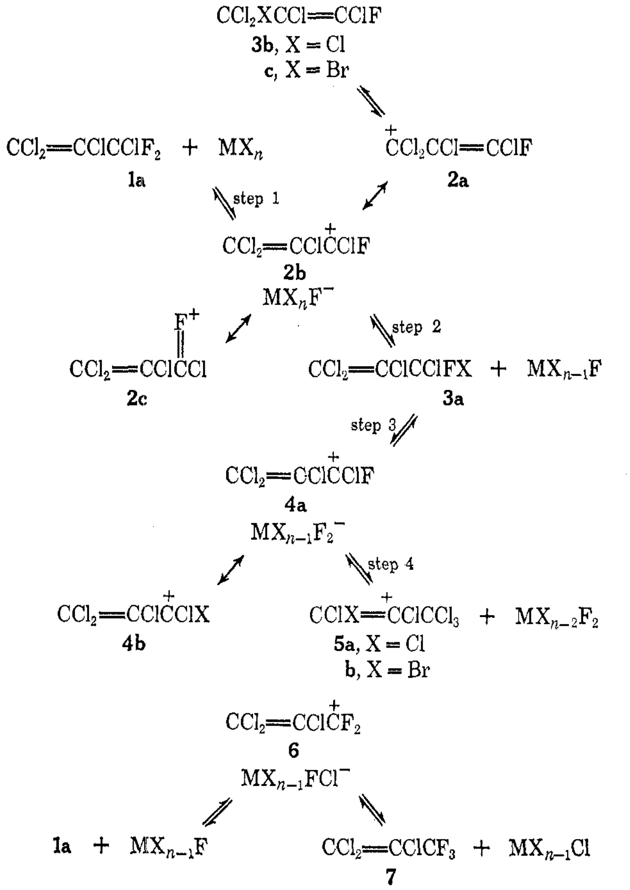
occurs between tetrachlorocyclopropene and the boron halides (or antimony trichloride), although the trichlorocyclopropenium cation was formed upon reaction with the chlorides of Al^{III}, Sb^{V}, and Fe^{III}.

Several reasons might account for this conflict with the literature activity sequence. An obvious difference between the previous study and this one is that of temperature, 128 and 50°, respectively. Although it is unlikely that this difference would alter the order of the activity sequence, it might account for the discrepancy in the case of ferric chloride.

Stirring was found to have a profound effect on the rate of disproportionation of **1a** with aluminum halides. With vigorous stirring the salt was soon dispersed as fine particles, whereas a gummy mass resulted from inefficient stirring. The surface area of the salt would be markedly different in the two cases, and would be expected to be of major importance in a heterogeneous reaction of this sort. Although mixtures were efficiently stirred in the present work, stirring is not mentioned in the previous report.

Mechanism.—A straightforward pathway for these reactions is outlined in Scheme I. A similar mechanism has been postulated for the vapor-phase disproportionation of dichlorofluoromethane on the basis of a kinetic study.[20] The formation of cation intermediates such as **2**, **4**, and **6** seems reasonable in view of the characterization of **4** as the tetrachloroaluminate and hexachloroantimonate salts.[16] Additional evidence of such cations is indicated by exchange of chlorine in the 1 and 3 positions of **5a** in the presence of aluminum chloride,[21] and the observation by nmr of 1,2,3-trichloropropenium tetrachloroaluminate in methylene chloride,[22] and of a variety of allylic and halogen containing cations.[23]

SCHEME I



With titanium and aluminum chlorides, the substitution process illustrated in steps 2 and 4 would continue until the metal is completely fluorinated, and the formation of the metal fluoride would be expected to provide a driving force for step 1. The position of equilibrium for step 1 in the reaction of antimony pentachloride, however, apparently lies well to the left. Step 3 could of course involve MX_n instead of $MX_{n-1}F$.

Resonance stabilization of cations by donation from fluorine[24] should be significant, and thus canonical form **2c** would be more important than **2a**. This reasoning is consistent with the report[3] that the disproportionation of **1a** with antimony pentachloride does not give 1-fluoropropenes, and that only the allylic chlorofluoro group was involved in the reaction. Hence, it would seem that only **3a** would be formed. A similar argument would hold in the case of **6**.

This mechanism seems fully adequate for the reactions of antimony pentachloride, titanium tetrachloride, and aluminum chloride; unfortunately, it does not readily account for the formation of $CF_3CCl{=}CClBr$ (**8**) and $CF_3CCl{=}CBr_2$ (**9**) from the reaction of aluminum bromide. Stepwise substitution of **1a** would lead first to $CFClBrCCl{=}CCl_2$, and then to $CClBr{=}CCl\text{-}CCl_2Br$ (**10**) and $CClBr_2CCl{=}CCl_2$ (**11**). It seems unrealistic to rationalize the formation of a substantial amount of **8** in terms of a random halogen exchange that would lead to the complete allylic fluorination of **10**. Such a process might seem plausible if **8** were present as only a trace amount, as is **9**, but that is not the case. An intermediate 1-bromo-3-fluoropropene such as **12** appears to be necessary to a plausible rationalization of the formation of **8**, since such an intermediate would readily disproportionate to **8**. An intermediate of this sort probably would not arise by Scheme I in quantities consistent with the final concentration of **8**, since an allylic shift to give a 1-bromo compound would not be expected to occur until removal of fluorine from the molecule were complete (step 4, X = Br).

Further, **12** must arise by yet another allylic shift in **3c**. Such rearrangements would be expected intuitively to be controlled by thermodynamic rather than kinetic factors, so that further rearrangement of **3c** would seem to conflict with any rationalization for its formation. However, **12** appears to be essential to a reasonable mechanism which gives rise to **8** *via* the reaction below; this process would require **12a** to be formed

$$3CClBr{=}CClCFClX \longrightarrow$$

12a, X = Cl
b, X = Br

$$\mathbf{8} + CClBr{=}CClCCl_2X + CClBr{=}CClCClX_2$$

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[20] E. Cavaterra, V. Fattore, and N. Giordano, *J. Catal.*, **8**, 137 (1967).

[21] F. Boberg, K. Kirchoff, and G. R. Schultze, *J. Label. Compounds*, **3**, 293 (1967); *Chem. Abstr.*, **68**, 95052 (1968).

[22] K. Kirchoff, F. Boberg, and D. Friedman, *Tetrahedron Lett.*, **25**, 2935 (1968); *Chem. Abstr.*, **69**, 76354 (1968).

[23] (a) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968); (b) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 947 (1968); G. A. Olah and Paul E. Petersen, *ibid.*, **90**, 4675 (1968).

[24] J. Hine, *ibid.*, **85**, 3239 (1963); J. Hine and F. E. Rogers, *ibid.*, **90**, 6701 (1968).

in at least 75% yield in order to give the quantity of **8** found experimentally. A 1-bromo-3,3-difluoropropene such as **13** formed in half that yield would give the amount of **8** found.

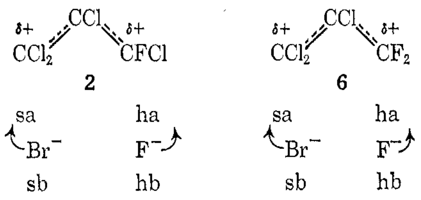
$$3CClBr{=}CClCF_2X \longrightarrow 2CClBr{=}CClCF_3 + CClBr{=}CClCX_3$$

$$\textbf{13a}, X = Cl \qquad \textbf{b}, X = Br$$

Most of the theoretical considerations which conflict with the formation of **12** apply to **13** as well; another more serious objection may be raised against postulation of this intermediate, however. Since the data in Table I indicate that conversion of aluminum bromide to the fluoride is complete, and since the analogous reaction with aluminum chloride is essentially complete in 1 hr, direct conversion to the fluoride would be more attractive from the standpoint of both thermodynamics and simplicity. Complete halogen exchange between aluminum bromide and perchloroolefins does occur,[18] however, and it is likely that the activation energy for the bromine–chlorine exchange would be lower than that of bromine for fluorine.

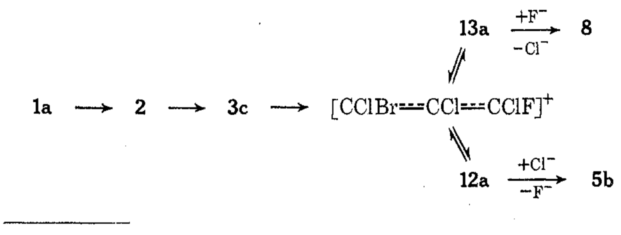
The exclusive initial coordination of fluorine by aluminum chloride has been demonstrated[25] in the rearrangement of $CF_2ClCFCl_2$; radioactive chlorine from the aluminum chloride was not contained by the rearranged CF_3CCl_3. This point is discussed more fully below.

From the involuted deduction above it is apparent that need exists for a simple, generally applicable concept which will account for the unexpected formation of **8**. In fact, the principle of hard and soft acids and bases (HSAB) advanced by Pearson[14] provides an explanation for the formation of **8**.



Intermediate ion **2** is seen as an ambident electrophile, in which $-C^+Cl_2$ is the softer electrophilic center. Thus, whenever opportunity exists, attack by F^-, a hard base (hb), will occur at the harder $-C^+FCl$, whereas Br^-, a soft base, will preferentially attack the *gem*-dichloro group. The most likely rationalization for the formation of **8** then would be the rapid initial reaction of aluminum bromide with **1a** to give **2** which is attacked by bromide yielding **3c**. This compound reacts further as shown in Scheme II. Ion **6** would not be expected to play a significant role in the formation of **8** because initial attack of aluminum bromide would be expected to occur on fluorine.

SCHEME II



Since **2** is attacked at $-C^+Cl_2$ by the soft Br^-, and at $-C^+FCl$ by the hard F^-, one might wonder whether the borderline base Cl^- would show a clear preference for one of these electrophilic centers. That is, might not attack of Cl^- on **2** lead to **3b** just as attack by Br^- yields **3c**? Examination of the infrared spectra of the product mixtures from the reaction of **1a** with Al^{III}, Ti^{IV}, and Sb^{V} chlorides, and from the reaction of aluminum chloride with **7**, failed to show the characteristic fluoroalkene absorption in the 1800–1600-cm^{-1} region. No rearranged olefins such as **3b** have been reported[3,8,26] in the reactions or preparation of **1a**.

HSAB and Other Systems.—In support of this mechanism predicted by the HSAB principle, it may be seen that many examples from the literature, which have been incompletely understood in the past, are more fully explained by this concept. Several similar allylic rearrangements have been reported; rationalization for many of these is lacking, although, as it will be shown, a consistent explanation is provided by HSAB theory.

The fluorination of 1,1,2,3,3-pentachloropropene (**14**) with antimony trifluoride[27] gives the three products indicated below, each in about 25% yield. When antimony pentachloride was added as a catalyst, the rearranged product **17** was formed in 92% yield. These results could be rationalized by the isomerization of **14** to the 1-hydro olefin by antimony pentachloride, except that **14** was unchanged upon treatment of antimony pentachloride alone. Clearly both antimony salts are necessary for the exclusive formation of **17**, although the reason for this requirement is not apparent. The equation below provides an understanding from HSAB concepts.

$$\underset{\textbf{14}}{CCl_2{=}CClCHCl_2} + SbF_3 \longrightarrow$$

$$\underset{\textbf{15}}{CCl_2{=}CClCHF_2} + \underset{\textbf{16}}{CHCl{=}CClCClF_2} + \underset{\textbf{17}}{CHCl{=}CClCF_3}$$

$$\textbf{14} \underset{+Cl^-}{\overset{-Cl^-}{\rightleftharpoons}} \underset{\text{ha}\quad \textbf{18} \quad \text{sa}}{[CCl_2C{=}{=}CCl{=}{=}CClH]^+} \underset{-F^-}{\overset{+F^-}{\rightleftharpoons}} \underset{\textbf{19}}{CCl_2FCCl{=}CClH}$$

Abstraction of chloride ion by antimony halide gives the ion **18**, as proposed by Whalley and Davis.[27] The $-C^+CCl_2$ group is a harder acid than $-C^+ClH$, owing to replacement of the soft base H^- in the latter by the harder Cl^-. Comparison of the two nucleophiles shows that F^- is harder than Cl^-, so that the former preferentially attacks the harder electrophilic center to give **19**. Further reaction of **19** forms another ambident ion which is attacked by F^- at the harder end, *i.e.*, $-C^+ClF$.

The addition of pentavalent antimony allows formation of a relatively long-lived ion so that the product reflects equilibration between the 1 and 3 positions; this does not occur with antimony trifluoride alone because it is a relatively weak Lewis acid. The fact that **14** is not isomerized by antimony pentachloride alone demonstrates that the limit of the symbiotic effect[14b]

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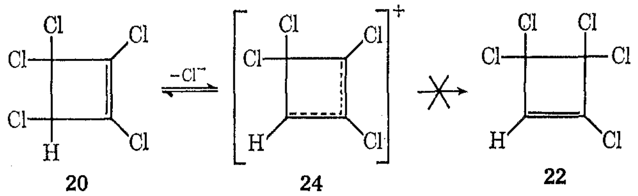
[25] W. T. Miller, Jr., E. W. Fager, and P. H. Griswald, *J. Amer. Chem. Soc.*, **72**, 705 (1950).

[26] A. L. Henne, A. M. Whalley, and J. K. Stevenson, *ibid.*, **63**, 3478 (1941).

[27] A. M. Whalley and H. W. Davis, *ibid.*, **70**, 1026 (1948).

has been reached. That is, the tendency of carbon in $-CCl_2^+$ to surround itself with chlorine atoms to form the $-CCl_3$ group is counteracted by steric effects. The facile rearrangements of 3,3,3-trichloropropene and 2,-3,3,3-tetrachloropropene to 1,1,3-trichloropropene and 1,1,2,3-tetrachloropropene, respectively, reported by Haszeldine follow this pattern, although the suggestion that 3,3-dichloro-3-fluoropropene rearranges to 1,1-difluoro-3-chloropropene seems open to question.[28]

Another similar example is the reaction of 2-chloro-3,3,4,4-tetrafluorocyclobutene with aluminum chloride[29] to give the 3-H isomer **20**. Although **22** should be favored because of the symbiotic effect, the steric interaction of the adjacent *gem*-dichloro groups apparently precludes the formation of **22**.

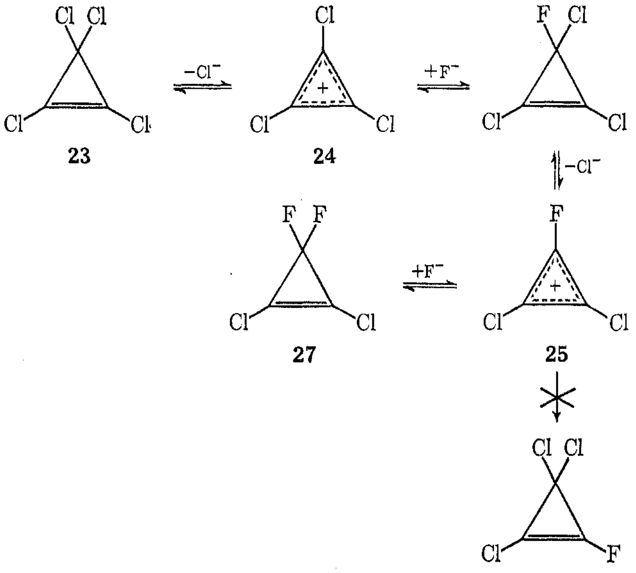


20 **24** **22**

Hine[24] has pointed out the profound effect of clustering of like atoms about the same carbon atom (the symbiotic effect in HSAB terminology) on the behavior of organic fluorine or oxygen compounds and has interpreted this effect in terms of double bond–no bond resonance. From the examples cited above it may be seen that such an effect is usually of less importance than steric factors in the case of allylic chlorine compounds.

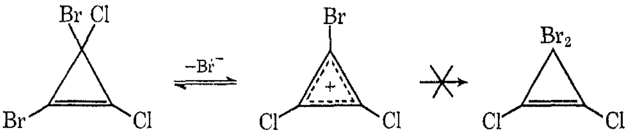
It is for this reason that **3b** and **1b** are not formed in readily detectable amounts in the reactions of **1a**, although by naive application of this HSAB concept one would expect these isomeric materials to be formed. It has been pointed out[24] that operation of double bond–no bond resonance (or the symbiotic effect) by halogens other than fluorine would not be likely. It may be seen then that neither approach is wholly successful in the rationalization of the reactions of **1a** since the formation of **8** may not be explained completely in terms of double bond–no bond resonance, and the formation of rearranged products **3b** and **1b** would be predicted by the HSAB concept of symbiosis. The rationalization presented in Scheme II is a fusion of the two approaches: the HSAB concept explains the formation of **12b**; and the concept of double bond–no bond resonance accounts for rearrangement of this compound to **12a**, since structures having the fluorine atom on a saturated carbon atom would be expected to provide more effective double bond–no bond resonance. It should be mentioned that in the absence of the concept of symbiosis, prediction of the position of attack of Cl^- on **2** from the HSAB principle would be difficult, since Cl^- is a borderline base and the difference in hardness between the two electrophilic centers would not be great.

The utility of HSAB concepts, however, is demonstrated in the reaction of tetrachlorocyclopropene with antimony trifluoride.[18b] The substitution would be predicted to cease after the introduction of the second fluorine atom since attack by fluoride ion on intermediate **25** would occur preferentially at the harder $>C^+F$ group. Further reaction would require removal of F^- from **27** which only regenerates **25**. That **26** is not formed by attack of Cl^- on **25** must again be attributed to more effective double bond–no bond resonance by fluorine at a saturated carbon atom. Tobey and West rationalized the behavior of **23** in this reaction in terms of double bond–no bond resonance.[18b]



23 **24** **27** **25** **26**

That reaction of **23** with boron tribromide does not cease after formation of the dibromide, but instead gives tetrabromocyclopropene,[18b] may be attributed in part to steric factors. Although attack by Br^- to give a *gem*-dibromo group would be favored by the symbiotic effect, this tendency is counteracted by steric interactions so that **29** is formed. Successive reaction of this sort leads to the fully substituted product. This argument would also apply to the reaction of hexachlorocyclopentadiene with boron tribromide.[18a] Another factor which probably comes into play in the reactions of **24** is discussed later.



The reaction of hexafluoropropene with aluminum chloride has been studied by Park, Hopwood, and Lacher who reported the following products in addition to starting material:[30] $CF_3CF{=}CFCl$ (**30a**), $CF_3CF{=}CCl_2$ (**31a**), $CF_2ClCF{=}CCl_2$ (**33a**), $CFCl_2CF{=}CCl_2$ (**34a**), $CCl_3CF{=}CCl_2$ (**35**). The **31a** and **35** were formed in much larger amounts than the others. Comparison of the mechanism postulated by these investigators with Scheme III, which represents the pathway derived from HSAB concepts for the conversion of the initially formed **30b** to **35**, reveals several significant differences. Whereas the former accounts for the formation of **31a** by rearrangement of $CF_2ClCF{=}CFCl$ through an unspecified route, Scheme III shows **31a**, as well as **30a**, to arise quite naturally from combination of the extremely hard acid $-C^+F_2$ with the hard F^- from a fluoroaluminate ion.

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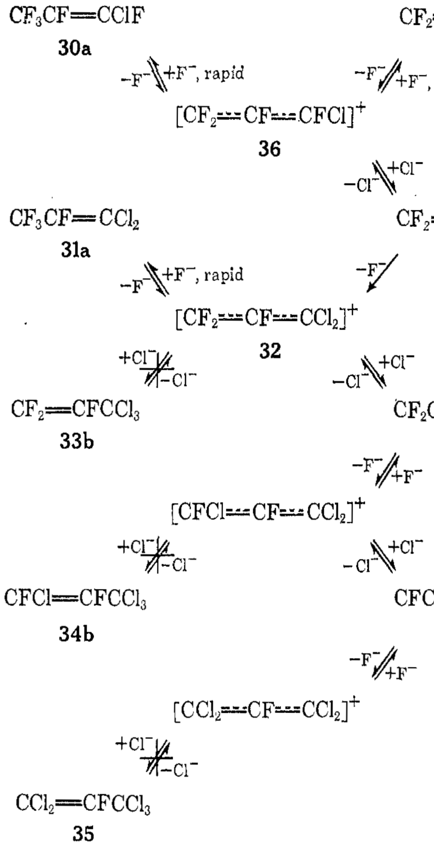
(28) R. N. Haszeldine, *J. Chem. Soc.*, 3371 (1953).

(29) K. V. Scherer and T. J. Meyers, *ibid.*, **90**, 6253 (1968).

(30) J. D. Park, S. L. Hopwood, and J. R. Lacher, *J. Org. Chem.*, **23**, 1169 (1958).

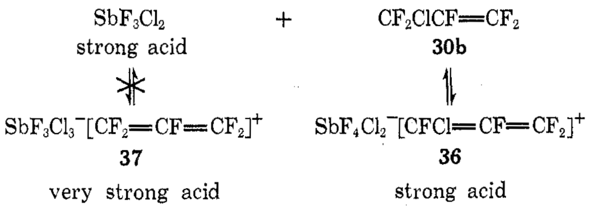
SCHEME III



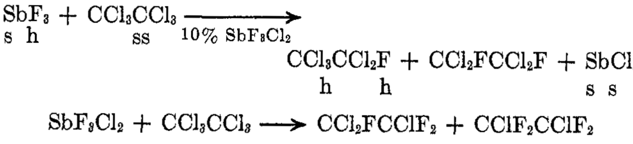
The resistance of these two materials to further substitution by Cl^- originates from the kinetics of the reaction, since the step which leads to each is an impasse in the substitution process. The olefins **33b**, **34b**, and **35** were not reported. The apparent reason for the difficulty in the replacement of the fluorine in **35** is that the fluorine is not in an allylic or potential allylic position, although this fact apparently was not fully appreciated in the past.[30]

The allylic rearrangement of $CF_2{=}CFCF_2Cl$ (**30b**) reported by Henne and Newby[31] brings up an important aspect of these reactions which has not been fully discussed. This compound was converted in 82% yield to the isomeric **30a** upon attempted fluorination with SbF_3Cl_2 and antimony trifluoride. Under similar conditions **31b** was also converted to **30a**.

It may be seen that these results are readily interpreted in terms of formation of the common intermediate **36**. The formation of **36** from **30b** seems inconsistent with previous examples, since antimony would be expected to preferentially abstract the softer base Cl^-. However, removal of Cl^- from **30b** would generate the very *strong* acid **37**, which is apparently a *stronger* acid than SbF_3Cl_2 and, in this case, the considerations of acid strength take precedent over those of hardness and softness. In the case of **31b**, SbF_3Cl_2 is a sufficiently strong acid, so that ion formation is determined as expected by hardness and softness considerations. It should also be remembered in this regard that F^- is a *stronger* base toward the proton than are the other halide ions.



HSAB and Saturated Compounds.—The effect of acid strength discussed above may be seen more clearly in the fluorination of aliphatic compounds with antimony salts. The reaction of hexachloroethane with antimony trifluoride[32] containing 10% SbF_3Cl_2 gives products containing the $-CCl_2F$ group, whereas reaction with SbF_3Cl_2 proceeds to the $-CClF_2$ group. Conversion of $-CCl_3$ to $-CCl_2F$ results not only in a harder group, but one which is a *stronger* acid as well. For this reason, reaction occurs in an alternate stepwise fashion, and ceases with the formation of the $-CClF_2$ group. That is, $CF_2Cl^+CF_2$ is a *stronger* acid than SbF_3Cl_2, just as $CF_2{=}CF^+CF_2$ is. The reaction of hexachloropropene proceeds to $CF_3CCl{=}CCl_2$ (**7**) with antimony trifluoride alone,[26] because removal of Cl^- from $CF_2ClCCl{=}CCl_2$ gives $[CF_2{=}CCl{=}CCl_2]^+$ (**6**), which is a weaker acid than either $[CF_2{=}CF{=}CF_2]^+$ (**37**) or $CF_2Cl^+CF_2$.



$$\underset{s\ \ h}{SbF_3} + \underset{ss}{CCl_3CCl_3} \xrightarrow[10\%\ SbF_3Cl_2]{} \underset{h}{CCl_3CCl_2F} + \underset{h}{CCl_2FCCl_2F} + \underset{s\ s}{SbCl_3}$$

$$SbF_3Cl_2 + CCl_3CCl_3 \longrightarrow CCl_2FCClF_2 + CClF_2CClF_2$$

That antimony pentachloride is ineffective as a catalyst for the disproportionation of saturated fluorochlorocarbons, as we have found with CF_2ClCCl_3, and as reported with CCl_3F and CCl_2FCCl_2F,[3] is consistent with this argument. These findings indicate that $SbCl_5$ is a weaker acid than SbF_3Cl_2, since the latter is strong enough to remove Cl^- from CCl_2FCCl_2F and CCl_2FCClF_2. The reactivity toward fluorination by antimony compounds suggests that the acid strength of various ions toward Cl^- in these reactions decreases in the order $C^+F_2CX_3$, $[CF_2{=}CX{=}CF_2]^+ > C^+FClCX_3$, $[CFCl{=}CX{=}CF_2]^+ > C^+Cl_2CX_3$, $[CCl_2{=}CX{=}CF_2]^+ > [CCl_2{=}CX{=}CClF]^+ > [CCl_2{=}CX{=}CCl_2]^+$; $X = F, Cl$; $-CX_3 = -CF_2Cl, -CFCl_2, -CCl_3$.

It may be noted from this arrangement that the softer, less acidic end of the ambident ions determines their acidity, and that the effect of the $-CF{=}CF_2$ group is approximately the same as that of a $-CF_2Cl$ or $-CFCl_2$ groups. The $-CCl{=}CCl_2$ group reduces the acid strength of an ion considerably, although an analogous group is not evident from this series. The parallel between these carbonium ion acidities and the reactivity of the parent compound toward disproportionation is readily apparent.

It should be pointed out that members of the ethane series are unstable toward intramolecular rearrangement of the sort described by Miller.[25,33] As mentioned above, radioactive chlorine from aluminum chloride was not incorporated by $CF_2ClCFCl_2$ during rearrange-

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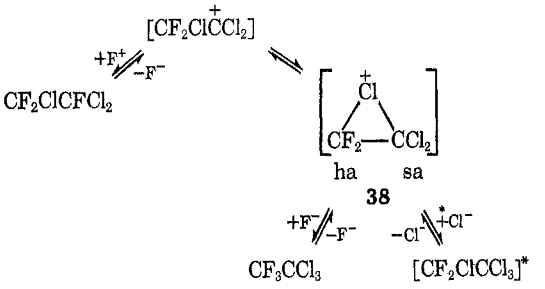
[31] (a) A. L. Henne and T. H. Newby, *J. Amer. Chem. Soc.*, **70**, 130 (1948). (b) Rearrangement of **30b** (or **30a**) to **31a** and hexafluoropropene at 400° over active aluminum fluoride is claimed by ref 3b.

[32] E. G. Lock, W. R. Brode, and A. L. Henne, *ibid.*, **56**, 1726 (1934).

[33] W. T. Miller, Jr., U. S. Patent Application 47,553; *Chem. Abstr.*, **47**, 4895 (1953); W. T. Miller, Jr., and E. W. Fager, U. S. Patent 2,598,411 (1952).

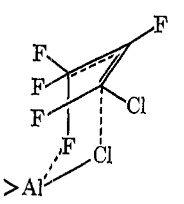
ment.[25] This fact strongly suggests the following mechanism for this reaction. Formation of halonium ions resembling **38** has been demonstrated by spectral and chemical means,[34] and intermediacy of such an ion in this case seems likely. Absence of this rearrangement during fluorination with SbF_3Cl_2 may be attributed to insufficient acid strength of SbF_3Cl_2, which would lead to a short-lived ion.



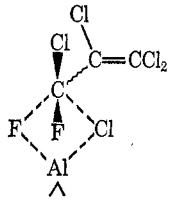
Another aspect of the acidity series should be mentioned. Since the trichlorovinyl group has such a pronounced effect on the acid strength of the cation, and because the π electrons of the trichlorovinyl group would increase the polarizability of the ion, it seems reasonable that the relative hardness of the ion would be altered. It seems likely, then, that the hardness of the $-C^{+}FCl$ group of $[CFCl{=}CCl{=}CCl_2]^{+}$ (**2**) might be reduced to a borderline classification. This softening effect would mitigate the symbiotic effect in the attack of Cl^- on **2**.

A similar effect would operate on cation **24**, which contains the dichlorovinyl group. This effect, coupled with steric factors, would tend to prevent the formation of **26**. Fluorination of this compound by a process of the sort observed in the reaction of hexachloroethane with SbF_3 might be expected to give complete substitution. For such a process to occur, however, a short-lived ion must be formed; this could hardly be the case with **24**, because it is probably an even weaker acid than **4**. Reaction of **24** with SbF_3 should give long-lived ions which would allow selective attack by nucleophiles.

Other Mechanistic Considerations.—The transition state in the substitution reactions involving rearrangement might well take the form of a six-centered configuration such as **43**, which represents the conversion of **30a** to **31b**. It may be seen that such an arrangement would not allow full overlap of p orbitals, although coplanarity of the *gem*-dihalo groups of the free ion would cause considerable steric interaction, particularly when chloro groups are involved.



43



44

In this regard, the ^{36}Cl exchange between the 1 and 3 positions of hexachloropropene and $Al_2{}^{36}Cl_6$ in solution may be mentioned;[21] reaction through a transition state similar to **43** would seem to provide a reasonable rationalization. It is interesting to note that ^{36}Cl exchange at the 2 position of **5a** is reported[21] to occur on solid aluminum chloride; this finding is consistent with the reaction of **35** with aluminum chloride[30] to give **5a**, although this reaction apparently only occurs under vigorous conditions.[30,35]

Although association of complex metal halide and carbonium ions to give a transition state similar to **43** would be required for reaction determined by HSAB considerations, *e.g.*, conversion of **1a** to **3c**, a non-HSAB reaction involving a four-centered transition state such as **44** would account for disproportionation and substitution reactions occurring without rearrangement, *e.g.*, **1a** to **7** and **3a**.

The nature of the metal halide would doubtless have a marked effect on the course of reaction; that is, reaction which occurs in solution could well follow a path different from that which occurs on the surface of a solid. That the aluminum fluoride formed in these reactions is an active catalyst may be attributed to a large number of lattice defects, which would result from the precipitation of aluminum fluoride from such a nonpolar medium. Such defects are usually well correlated with catalyst activity.[5,6,7,36]

Synthesis of 1-Bromo-1,2-dichloro-3,3,3-trifluoropropene (8).—The route devised to this compound was preparation of 1,2-dichloro-3,3,3-trifluoropropene (**17**), and bromination of this compound followed by its dehydrobromination. The reaction of **7** with zinc in formamide is reported[37] to give **17**. When this procedure was followed, the lower boiling isomer of **17** predominated. Separation of this material from 1,1-dichloro-3,3,3-trifluoropropene was not practicable, however, and the amount of the higher boiling isomer was too small to be useful.

Reduction of **7** with sodium borohydride was therefore undertaken. This reaction provided predominantly the high-boiling isomer of **17** which was readily purified. The proton nuclear magnetic resonance spectra of these compounds show a quartet (J_{HF} = 1.2 Hz) at δ 7.13 for the lower boiling compound and a broadened peak ($J_{HF} \leq 0.2$ Hz) at δ 6.65 for the higher boiling isomer. Other investigations[38] have shown J_{HF} to be greater in the case of the *cis* isomer. On this basis, we believe the higher boiling compound to be *trans*-1,2-dichloro-3,3,3-trifluoropropene and the lower boiling material to be the *cis* isomer, although this assignment conflicts with a previous one,[37] and with the usual relationship of boiling points of *cis–trans* isomers.

Bromination of **17**, followed by treatment with aqueous sodium hydroxide gave **8** whose retention time and infrared spectrum matched those of material isolated from the reaction of **1a** with aluminum bromide.

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[34] (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 6082 (1968); (b) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967).

[35] R. N. Sterlin, V. A. Siderov, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Otd Khim. Nauk*, 62 (1959); *Chem. Abstr.*, **53**, 14916 (1959).

[36] J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis," Academic Press, New York, N. Y., 1967.

[37] W. G. Finnegan and W. P. Norris, *J. Org. Chem.*, **28**, 1139 (1963).

[38] A. A. Bothner-By, S. Castellano, and H. Gunther, *J. Amer. Chem. Soc.*, **87**, 2439 (1965); J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965); W. R. Cullen, D. S. Dawson, and G. E. Styan, *Can. J. Chem.*, **43**, 3392 (1965); W. R. Cullen and W. R. Leeder, *Inorg. Chem.*, **5**, 1005 (1966); D. J. Burton, R. L. Johnson, and R. T. Bogan, *Can. J. Chem.*, **44**, 635 (1966).

Experimental Section

Apparatus.—Glpc data were obtained using an F & M Model 720 or Model 700 gas chromatograph equipped with thermal conductivity detectors. Analyses of products from reactions of **1a** were carried out using 10% SE-30 0.25 in. × 2 ft stainless steel column (column A) with a flow rate of 40 ml min^{-1} at a temperature programmed from 100 to 170° at 15° min^{-1}. Preparative glpc was performed using an F & M Model 720 fitted with a 0.5-in.-o.d. column or a Model 770 with a 0.75-in.-o.d. column. The glpc data in Table I are percentages from internal normalization which have been corrected to mole percentages with calibration curves. The amount of **1a** was then obtained by difference, and was in good agreement with the value obtained using *n*-decane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 21 or on a Perkin-Elmer Infracord. Melting points were determined using a modified Hershberg apparatus, and are corrected. Boiling points were determined during fractional distillation and are uncorrected. Transfers and weighings of anhydrous inorganic halides were accomplished in a drybox under an atmosphere of nitrogen.

Reactions between organic and inorganic halides were carried out in sealed ampoules which contained a magnetic stirring bar and were supported by a rack mounted over an air-driven magnetic stirrer. This entire apparatus was immersed in a well-stirred oil bath which was thermostated at 50 ± 0.5°.

Materials.—Aluminum chloride (J. T. Baker Chemical Co., 99.1% stated purity) was sublimed under vacuum and ground to a fine powder in an agate mortar in a drybox. Aluminum bromide (Fisher Scientific Co., 99%) was similarly ground. Boron tribromide (American Potash and Chemical) was treated with mercury and fractionally distilled under vacuum before use. Antimony pentachloride (Baker and Adamson Reagent), titanium tetrachloride (Matheson Coleman and Bell), aluminum fluoride (Matheson Coleman and Bell), antimony trifluoride (Ozark-Mahoning), 1,1-difluorotetrachloroethane (Hynes Chemical Co.), and sodium borohydride (Metal Hydrides Co.) were used directly.

Hexachloropropene (Eastern Chemical) was distilled under vacuum before use; glpc analysis of the distillate showed the presence of 5+% higher boiling impurities. Prolonged treatment of the distillate with concentrated aqueous potassium hydroxide reduced the amount of these contaminants to 0.5%. Preparative glpc (0.75 in. × 8 ft 10% SE-30) at 190° with a flow rate of 500 ml/min^{-1} nitrogen gave pure material: bp 92–93° (16 mm), lit.[3] bp 93.0–93.4° (16 mm), ir 1553 cm^{-1} (C=C).[39]

3,3-Difluorotetrachloropropene (1a).[4,8]—Antimony trifluoride (986 g, 5.5 mol) was placed in a 3-l. three-necked flask fitted with a mechanical stirrer, a pressure-equalized dropping funnel, and a column (40 cm × 19 mm od) which was connected in turn to an elbow, a water-cooled condenser, and a vacuum take-off adapter terminating in a 1-l. receiver. The funnel was charged with hexachloropropene (1494.0 g, 6.0 mol, 99.5%) which had been treated with potassium hydroxide. The system was evacuated to 140 mm by a water aspirator, and the flask was heated to 135° in an oil bath. The olefin was added over a period of 5 min.

When distillation under these conditions ceased, the distillate was poured into dilute hydrochloric acid, and the organic layer separated. The suspension of antimony salts was treated with an amount of 12 *N* hydrochloric acid just sufficient to dissolve the precipitate. The organic material freed by this treatment was combined with the first portion. The crude product was washed with three 250-ml portions 1 *N* hydrochloric acid and one 250-ml portion water; it weighed 954.7 g. Treatment with cold concentrated aqueous ammonia gave 18.7 g of 2,3,3-trichloroacrylamide. The olefin mixture was washed with water, dried (Na_2SO_4), and fractionated through a 30-cm glass helix packed column to give (a) 211 g, bp 89–125.7° (95% **1a**, 5% **7**); (b) 420.8 g, bp 125.7° (99.5% **1a**), n^{20}_{D} 1.4572, ir 1592 cm^{-1} (C=C) (lit.[3] bp 128.3°, n^{20}_{D} 1.4575); (c) 96.0 g, mid-cut (22% **1a**, 79% **3a**); (d) 167.3 g, bp 169.7° (99.5+% **3a**), n^{20}_{D} 1.5053, ir 1570 cm^{-1} (lit.[3] bp 170.1° n^{20}_{D} 1.5052), and (e) 15.7 g residue. These results (35% yield **1a**, 13% yield **3a**) are consistent with those obtained from several repetitions of this procedure.

2,3,3-Trichloroacrylyl Fluoride, $CCl_2{=}CClCOF$.—This material was isolated from fractions of **1a** prepared as above except that the ammonia treatment was omitted. Preparative glpc (10% Fluorosilicone DCQF-1 0.5 in. × 10 ft) at 65° gave material which was pure by glpc, and which had the following properties: n^{20}_{D} 1.4841; ir 1810 cm^{-1} (C=O), 1550 cm^{-1} (C=C). The 1250–650-cm^{-1} region of the ir spectrum closely resembled that of 2,3,3-trichloroacrylic acid.

This compound has a pungent, irritating odor and has a markedly deleterious effect on the sense of smell. Full olfactory acuity may not be regained for a period of 48 hr or more after a brief exposure.

2,3,3-Trichloroacrylamide, $CCl_2{=}CClCONH_2$.—The solid obtained from the treatment of crude **1a** with ammonia was collected on a filter and pressed dry. One recrystallization from 5:1 water–ethanol followed by vacuum drying gave fine white needles: mp 98.0° (lit.[40] mp 96–97°).

Anal. Calcd for $C_3H_2Cl_3NO$: C, 20.66; H, 1.16; N, 8.03. Found: C, 20.72; H, 1.30; N, 7.87.

2,3,3-Trichloroacrylic Acid.—A sample of hexachloropropene on prolonged exposure to the atmosphere was converted to large crystals which were acidic to litmus and congo red. One recrystallization from methanol–hexane (Skellysolve B) followed by air drying gave white crystals: mp 75–76° (lit.[41] mp 76, 74–75, 73, and 72.9°); ir (CCl_4) 2970–2550 (CO_2H), 1750, 1700 (C=O), 690 (C-Cl); ir (Nujol mull) 1720 (C=O), 1550 cm^{-1} (C=C).

Reaction of 1a with Metal Halides.—Inorganic halide (typically 0.010 mol) was transferred in a nitrogen-filled drybox to an ampule (20 mm o.d. × 150 mm with a neck 12 mm o.d. × 140 mm) which contained a Teflon-coated magnetic stirring bar (0.25 in. o.d. × 3/8 in.). Samples of aluminum chloride and bromide were weighed on tared 60-mm squares of aluminum foil, which assisted in dissipating static charges. Samples of antimony pentachloride, titanium tetrachloride, and boron tribromide were weighed by difference from excess liquid contained in a hypodermic syringe.

The ampoule was stoppered, removed from the drybox, and cooled in a Dry Ice bath. A gentle stream of nitrogen swept the ampoule during cooling. A weighed sample of **1a** (typically 21.60 g, 0.100 mol) was added, and the ampoule was sealed. The reaction mixture was stirred and heated in the apparatus described. At the end of the time specified, the mixture was poured into approximately 20 ml water and was vigorously stirred. The organic layer was separated and washed with three 10-ml portions of 1 *N* hydrochloric acid and one 10-ml portion of water. The sample was dried (Na_2SO_4) and analyzed by glpc as described above.

The aluminum chloride became bright yellow on contact with **1a**, but this color was soon replaced by a dull red-brown. After stirring a short time (*ca.* 0.5–1.0 hr), the solid was converted to very fine black particles which were dispersed almost to the top of the liquid. Aluminum bromide behaved similarly except that it was initially a deep red and had marked tendency to adhere to the ampoule and the stirring bar.

The titanium tetrachloride reaction mixture remained homogeneous for 20 min; at the end of this time a heavy brown suspension formed. The solid remained dispersed uniformly throughout the liquid for the remainder of the reaction; after a few hours, it had become a grassy-green color.

Reaction mixtures of **1a** with antimony pentachloride and with boron tribromide remained homogeneous and without visible change.

Gravimetric Chloride Analysis.—Aluminum chloride and **1a** were allowed to react for 1 hr as described above. The reaction mixture was then treated with 25 ml of distilled water, and the organic layer was separated and twice washed with 25-ml portions of water. The combined aqueous extracts were treated with 30 ml of a solution *ca.* 0.1 *M* in silver nitrate. The precipitate coagulated, collected in a dried and tared sintered-glass funnel, and washed with three portions (5–10 ml each) of 0.01 *N* nitric acid. It was dried to constant weight at 110–115°; the data are summarized below.

	1a, g	Al_2Cl_6, g	AgCl, g	Al_2Cl_6 remaining, %
Trial 1	21.60	1.3316	0.0423	0.99
Trial 2	21.60	1.3603	0.0614	1.40

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[39] It may be noted that Sadtler's Standard Spectra (#4655) shows extraneous bands at 2950 and 1750 cm^{-1}, which are indicative of trichloroacrylic acid or its derivatives.

[40] "Beilstein's Handbuch," **H2**, 402.

[41] E. H. Huntress, "Organic Chlorine Compounds," Wiley, New York, N. Y., 1948, p 236.

Isolation of 1-Bromo-1,2-dichlorotrifluoropropene (8), $CF_3CCl{=}CClBr$.—Compound **1a** (13.9 g, 0.0644 mol) was added to aluminum bromide (8.60 g, 0.322 mol) in a 50-ml flask surrounded by an ice–water bath. The mixture was then stirred and heated at 50 ± 5° under an atmosphere of nitrogen for 16 hr. The mixture was hyrolyzed, and the organic material washed with water and dried. The crude product, which contained *ca.* 7% of the first-eluted unknown compound, was subjected to simple distillation to remove high-boiling compounds.

The distillate was separated by preparative glpc (15% SE-30 0.5 in. × 10 ft) at 70° with a flow rate of 300 ml min^{-1}. The sample of the first-eluted unknown compound gave a single peak on column A: ir 1585 cm^{-1} (C=C), 1269, 1200, and 1156 cm^{-1} (CF_3), 999, 883, 798, 791, 688, 667 cm^{-1} (C–C, C–X).

Anal. Calcd for $C_3BrCl_2F_3$: C, 14.77; H, 0.00. Found: C, 15.40; H, 0.68.

A small sample of the second-eluted unknown compound was collected, and gave a single peak on column A: ir 1565 (C=C), 1258, 1193, and 1153 (CF_3), 986, 827, 776 cm^{-1} (C–C, C–X).

Preparation of 17.—Compound **7** (199.5 g, 1.0 mol) and 200 ml of diethylene glycol dimethyl ether (diglyme) were placed in a 2-l. three-necked flask fitted with a thermometer, a pressure-equalized dropping funnel, and a water-cooled condenser, which was in turn connected to a mercury–acetone bubbler. The solution was cooled to 0° in a 1-propanol–Dry Ice bath, and a solution of sodium borohydride (19.3 g, 0.50 mol 98% purity) and water (27.0 g, 1.5 mol) in 600 ml of diglyme was added over a period of 1 hr. Temperature during the addition was maintained at 10–15°.

The mixture was allowed to stir at room temperature for 36 hr after the addition was complete; it was then poured into 2 l. water with vigorous stirring. The organic layer was separated, washed with water, and dried. Fractionation through a 45-cm spinning-band annular still (Column A) gave (a) 14.4 g, bp 55.0–56.0°, *cis*- and *trans*-**17** containing a trace of 2-chloro-3,3,3-trifluoropropene; (b) 4.8 g, bp 56.0–60.5°, *cis* and *trans* **17**; and (c) 5.6 g, bp 60.5–61.5°, *trans* isomer of **17**, 99.5+% by glpc.

This procedure was repeated as above, except that the water was contained in the olefin solution. Analysis of the crude mixture by glpc on column B at 25° showed 2-chloro-3,3,3-trifluoropropene 4.3%, low-boiling **17** 7.2%, high-boiling **17** 27.4%, and starting olefin 60.8%. Fractionation through column A gave samples of each geometric isomer of 99.9% purity of *cis*-1,2-dichloro-3,3,3-trifluoropropene: bp 55.5° (750 mm), n^{20}_{D} 1.3672; nmr δ 7.13, J_{HF} = 1.2 Hz [lit.[37] bp 51–52° (702 mm), n^{20}_{D} 1.3638; nmr δ 7.08, J_{HF} = 1.1 Hz]; ir 1629 cm^{-1} (C=C), 1307, 1205–1160 cm^{-1} (CF_3); high-boiling **17**, bp 60.0° (742 mm), n^{20}_{D} 1.3768; nmr δ 6.65, J_{HF} ≤ 0.2 Hz [lit.[37] bp 58° (702 mm), n^{25}_{D} 1.3795; nmr δ 6.65, J_{HF} = 0.2 Hz]. Recovery of starting olefin was 90.8 g.

Bromination of 17.—Bromine (10.1 g, 0.063 mol) and 1,2-dichloro-3,3,3-trifluoropropene (10.4 g, 0.063 mol 91% high-boiling isomer, 9% low-boiling isomer) were placed in a flask, which was equipped with a water-cooled condenser and a magnetic stirring bar. The mixture was irradiated by an ultraviolet lamp from a distance of 15 cm for 72 hr. Analysis by glpc on column A indicated the absence of starting olefin, although the color of bromine persisted in the reaction mixture. The crude 1,2-dibromo-1,2-dichloro-3,3,3-trifluoropropane (**45**) was washed with water and used without further purification.

Dehydrobromination of 45.—Dibromide **45** was treated with a solution of sodium hydroxide (2.90 g, 0.070 mol 97% purity) in 15 ml of water with vigorous stirring for 3 hr. The organic halide was separated, washed with water, and dried ($MgSO_4$). Fractionation through a 12 × 150 mm Vigreux gave 4.8 g **8**: bp 108.0° (740 mm), n^{20}_{D} 1.4402; ir 1582 cm^{-1} (C=C), 1267, 1196, 1156 cm^{-1} (CF_3), 998, 876, 796, 789, 689, 665 cm^{-1} (C–C, C–X); 99.9+% pure by glpc. A small fraction, 0.25 g, bp 108.0°, containing 1.5% low-boiling impurity was also obtained; the residue weighed 4.0 g.

Anal. Calcd for $C_3BrCl_2F_3$: C, 14.77; H, 0.00; Br, 32.77; Cl, 29.07; F, 23.37. Found: C, 15.16; H, 0.00; Br, 32.90; Cl, 27.63; F, 23.70.

Registry No.—**1a**, 431-50-5; **8**, 25055-21-4; *cis*-**17**, 25062-10-6; *trans*-**17**, 25062-11-7.

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Triarylphosphine-Catalyzed Dimerization of Acrylonitrile and Related Reactions

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In the triarylphosphine-catalyzed dimerization of acrylonitrile to 2-methyleneglutaronitrile (I) and 1,4-dicyano-1-butene (II), the importance of a proper balance between nucleophilicity of the phosphine catalyst and protolytic strength of the solvent is delineated. Best results (85% yield of a mixture of 68% I and 32% II at 36% conversion of acrylonitrile) are obtained with a tri(*p*-tolyl)phosphine catalyst in triethylsilanol solution at 160°. Reaction of methyl vinyl ketone with a triphenylphosphine catalyst in triethylsilanol solvent gives only one catalytic dimer, 3-methylene-2,6-heptanedione, in 78% yield. Treatment of equimolar amounts of acrylonitrile and ethyl acrylate with a tributylphosphine catalyst at 100° affords only one cross-condensation product, 2-carbethoxy-4-cyano-1-butene, despite the fact that two cross-condensates are possible.

Recently, Baizer, and Anderson[1] have described a novel triphenylphosphine-catalyzed dimerization of acrylonitrile to a mixture of 60% 2-methyleneglutaronitrile (I) and 40% 1,4-dicyano-1-butene (II). The reaction was carried out at 45° in the presence of a small amount of *t*-butyl alcohol and only a 9% conversion of acrylonitrile to dimers was observed after 198 hr. We discovered[2] this reaction independently and now describe our results which show the triarylphosphine-catalyzed dimerization to be of significantly greater value[3] for the synthesis of II than implied by Baizer and Anderson.

Both the conversion of acrylonitrile and the yields of I and II vary significantly with the reaction temperature, the nature of the triarylphosphine, and the solvent. The results in Table I show that in *t*-butyl alcohol solvent at 175°[4] with triphenylphosphine as a catalyst, only a 45% yield[5] of dimers (I + II) at 15% conversion of acrylonitrile is obtained. The principal by-products are an insoluble crystalline hexamer[6] (15–20%) and soluble polymer (25–30%). When tri(*p*-

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[1] M. M. Baizer and J. D. Anderson, *J. Org. Chem.* **30**, 1357 (1965).

[2] J. D. McClure, U. S. Patent 3,225,083 (1965).

[3] The synthetic value of the tributylphosphine-catalyzed dimerization which produces I, exclusively, was emphasized by Baizer and Anderson.[1]

[4] At temperatures greater than 175°, the thermal dimerization to 1,2-dicyanocyclobutane becomes significant.

[5] Yields are based on converted acrylonitrile.

[6] N. Takashina and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 489 (1962).