

for 15 min. The separated etherphase was washed with aqueous solutions of sodium bisulfite and sodium carbonate and then dried. Removal of the ether left crude *p*-toluenesulfonyl-¹⁸O chloride (28.4 g, 74%). It was recrystallized four times from petroleum ether (bp 30–60°) and formed a white crystalline mass (23.5 g, mp 66–67°, lit.⁴⁶ mp 69°). The sulfonyl chloride was then converted to *p*-toluenesulfonyl-¹⁸O-hydrazine (86%, mp 107–108°, lit.⁴⁷ mp 112°) by reaction with hydrazine (95%) in benzene. The product was recrystallized from ether. Mass spectral analysis of **4'** indicated it contained 0.5% atom excess of ¹⁸O. Reaction of **4'** with sodium methoxide in NMP gave **10** and **11** as before. The alcohols were collected during gc analysis and a mass spectral analysis of them gave an ¹⁸O atom excess of 0.4 and 0.6% in two trials.

Decomposition of Tosylhydrazone **4 in Other Solvents.** (a) Decomposition of **4** (1 g, 3.42 mmoles) in hexadecane (15 ml) at 180° using sodium methoxide (0.2 g, 3.76 mmoles) *under air* for 15 min led to the precipitation of sodium *p*-toluenesulfinate (positive mercuric chloride test). Gc analysis of the reaction material *directly* indicated aldehyde **23** (53.5–57% over several runs), but *no* alcohols **10** or **11**. Another reaction as above (but on a one-fifth scale) *under nitrogen* again gave sodium *p*-toluenesulfinate, but *no* volatile products other than solvent were detected by gc analysis of the unprocessed material. (b) Identical experiments on **4** using diethyl Carbitol yielded similar results. An experiment using a mixed solvent of diethyl Carbitol and an amount of NMP equivalent to **4**, however, again yielded alcohols **10** and **11**, though the yield was lowered to 25%. (c) Tosylhydrazone **4** (1 g), sodium methoxide (0.2 g), and pyridine N-oxide (10 g) were held at 180° for 20 min and then poured into excess dilute hydrochloric acid. The acidic solution was thoroughly extracted with petroleum ether and the extracts were dried and concentrated. Treatment with 2,4-DNP reagent afforded the derivative of **23**, which was recrystallized from ethanol, mp 187–188° (*vide supra*, mp 191–193°). The previously mentioned acidic solution was made alkaline (odor of pyridine) and again extracted with petroleum ether. The extracts were combined, dried, and concentrated. Upon the addition of a concentrated ethanolic solution of picric acid, pyridinium picrate formed (mp 145–150°, unchanged upon repeated recrystallizations from ethanol, lit.⁴⁸ mp 167°). The infrared spectra of

the derivatives were identical with knowns. The yields of the derivatives were high, but not measured. (d) Reaction of **4** (1 g) with sodium ethylene glycolate (1 *N*, 5 ml) at 180° was complete within 2 min with quantitative evolution of nitrogen. The material was poured into water and extracted with petroleum ether. Isolation of the major gc peak material gave a colorless oil, λ_{max} 2.9 (O–H), 8.99 (>C–O) 9.4 (br, –CH₂–O–), which was neither **10** nor **11**. Its spectrum suggests it was **26**, though the compound was not investigated further to prove this.

Cleavage of Sulfinic Esters.—While the complete description of these reactions will be published later,^{18,33} one critical experiment may be described. Sulfinic esters **18** (60.4 mg) and **24** (314 mg) were heated *alone* in NMP (about 0.5 ml) for 2 min. The black reaction mixture was transferred quantitatively with acetone to a 10-ml volumetric flask and diluted to the mark with further acetone. Quantitative gc analysis (using peak area *vs.* micromoles calibration curves for each alcohol) indicated a yield of **10** and **11** of 73.8, 70.1, 71.9, and 73.7% (four separate analyses, av 72.4%). The infrared spectrum of the collected alcohols matched that of the alcohol mixture from **4** excellently, leading to the ratio (Table I) of 5.2 parts of **10** to 1 part of **11**. Nmr analysis gave a ratio closer to 7 parts of **10** to 1 part of **11**. Heating ester **18** (400 mg) in hexadecane (5 ml) at 180° for 15 min yielded no detectable sulfone **29** nor *p*-toluenesulfinic acid (failure of mercuric chloride test on aqueous wash). No alcohol was observed by infrared methods at this time, but later work³³ has shown the alcohol is formed to a slight extent (*ca.* 3% by gc). The failure to observe sulfone formation is in keeping with literature results⁴⁹ where only those sulfinic esters capable of yielding more stable carbonium ions by C–O cleavage are rearranged thermally to sulfones.

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(46) R. L. Shriner, R. C. Fuson, D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 380.

(47) K. Freudenberg and F. Blümmel, *Ann.*, **440**, 45 (1924).

(48) See ref 46, p 335.

(49) Cf. D. Darwish and R. McLaren, *Tetrahedron Letters*, 1231 (1962); D. Darwish and E. A. Preston, *ibid.*, 113 (1964); D. Darwish and J. Noreyko, *Can. J. Chem.*, **43**, 1366 (1965).

Heterogeneous Defluorination of Carbon

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A variety of fluorinated olefins have been found to undergo halogen interchange in the presence of a solid Lewis acid. Cyclic olefins such as perfluorocyclobutene are converted to their perchloro analogs by the action of aluminum chloride with particular ease. This same reaction does not appear to proceed in the homogeneous phase.

During a search for methods of cleavage of the very strong carbon–fluorine bonds, a route which appears to have some generality has been examined. The early literature indicates that dichlorodifluoromethane in benzene evolves hydrogen fluoride upon addition of aluminum chloride.¹ Trichlorofluoromethane forms carbon tetrachloride very rapidly in the presence of aluminum chloride. Aluminum chloride has been shown to produce a variety of fluorochloropropenes when it is treated with hexafluoropropene.^{2,3} A

Lewis acid such as boron tribromide has been found to replace all of the chlorine or tetrachlorocyclopropene.⁴ Although the latter reaction involves cleavage of the carbon–chlorine bond rather than the carbon–fluorine bond, it appears to be related to the preceding examples in a general way.

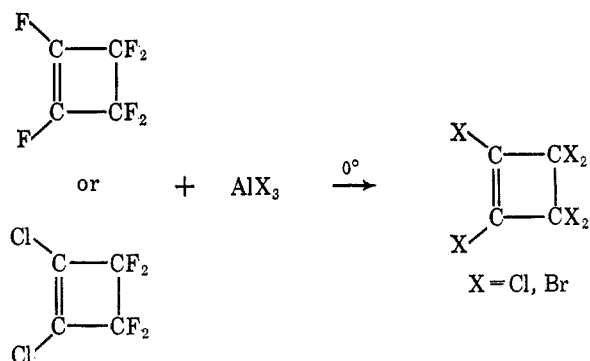
The present study concerns the reaction of acyclic and cyclic fluorine containing olefins with Lewis acids. We have observed that interconversion of halogen takes place rapidly when cyclic fluorine containing olefins are mixed with either aluminum bromide or aluminum chloride.

(1) A. L. Henne and H. M. Leicester, *J. Am. Chem. Soc.*, **60**, 864 (1938).

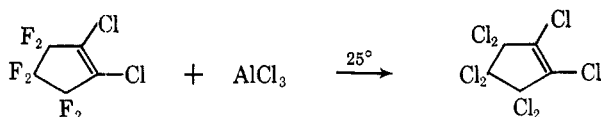
(2) J. D. Park and S. L. Hopwood, *J. Org. Chem.*, **23**, 1169 (1958).

(3) R. Sterlin, V. A. Disorov, and I. L. Knunyants, *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 62 (1959).

(4) W. S. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964).



At low temperatures, aluminum chloride and aluminum bromide are found to react with hexafluorocyclobutene to produce hexachlorocyclobutene and hexabromocyclobutene, respectively. The generality of this reaction and its relationship to the findings of Tobey and West is demonstrated by the fact that 1,2-dichlorotetrafluorocyclobutene also gives the same products with these two Lewis acid reagents.⁵ A five-membered fluorinated olefin behaves in an analogous fashion.



Aluminum chloride reacts with 1,2-dichlorohexafluorocyclopentene to produce octachlorocyclopentene, exclusively. Aluminum bromide with the aforementioned cyclopentene gives a dichlorohexabromocyclopentene. However, the location of the double bond in the latter compound is still somewhat in doubt. Under the same reaction conditions, aluminum chloride reacts with the carbon-fluorine bonds of perfluorocyclohexene to give a good yield of hexachlorobenzene. In the seven preceding reactions, progress to fully chlorinated or brominated products takes place so rapidly that intermediate materials are not isolated.

The results with perfluoropropene^{2,3} led us to believe that an acyclic system requires more stringent conditions for defluorination. Indeed, this turns out to be the case. Experiments have been performed with the combination perfluorobutene-2 and aluminum chloride. A mixture of 75% *trans*- and 25% *cis*-perfluorobutene-2 has been used in all experiments. The interaction with this fluoroalkene gives drastically different results depending upon the reaction temperatures. Thus, no reaction was obtained at 25°. At 80°, the products were the *cis-trans* isomers of 2,3-dichlorohexafluorobutene-2 (67% *cis*, 33% *trans*), 1,1,1-trifluoropentachlorobutene-2, and hexachlorobutadiene. At 110°, the main reaction products were hexachloroethane and hexachlorobenzene. It is interesting to note that in the case of the 2,3-dichlorohexafluorobutene-2, the relative amounts of the *cis-trans* isomers are reversed from that of starting material. At the higher temperatures, a fragmentation-condensation reaction takes place along with the halogen interchange. The net result of this occurrence is that more unsatura-

(5) It is interesting to note that we were unable to convert hexachlorocyclobutene to hexabromocyclobutene by action of either AlBr_3 or BBr_3 . Evidently there is somewhat less reactivity to Lewis acids in the cyclobutenyl system than in the comparable cyclopropenyl case.⁴

tion is introduced and a fully chlorinated butene derivative is not isolated.

Variations of these reactions were noteworthy for their lack of success. Attempted interactions of perfluorocyclobutene with boron trichloride, boron tribromide, and antimony pentachloride did not give cleavage of the C-F bond. Further, reactions of 1,1-dichlorodifluoroethylene, chlorotrifluoroethylene, and 1,1-difluoroethylene with aluminum chloride or aluminum bromide also failed. It had been noted earlier³ that the central fluorine in hexafluoropropene cannot be replaced. From these experiments it can be concluded that C-F bond cleavage is heterogeneous and best takes place on the acidic surface of an aluminum halide. Further, only olefins which contain a fluorine in a potential allylic position appear to be reactive.

Experimental Section

Hexachlorocyclobutene.—Anhydrous aluminum chloride (5 mmoles) was added to a 400-psi test glass vessel fitted with a brass vacuum-pressure valve. The vessel was evacuated to 10- μ pressure for 30 min, and 5.0 mmoles of hexafluorocyclobutene was transferred into it. The vessel was pressurized with an excess (30 mmoles) of anhydrous hydrogen chloride after cooling to -80° . The contents were held at 0° for 12 hr. After completion of the reaction, an ice-water slurry was added, and the mixture was extracted with trichlorofluoromethane. The organic layer was dried with CaCl_2 and filtered and the solvent evaporated. The residue was a white crystalline solid which melted at $51-53^\circ$ (3.84 mmoles, yield 77%). Sublimation followed by recrystallization from methanol gave the analytical sample which had the form of white plates, mp $51-52^\circ$. The infrared spectrum showed bands at 1620, 1180, 900, 785, 665 cm^{-1} . Molecular weight by the Rast method was 256 and the boiling point elevation gave a value of 255, theoretical 261. This material had the same infrared spectra and melting point as that reported by Howald.⁶

Essentially the same procedure was followed in the preparation of hexachlorocyclobutene from hexafluorocyclobutene in the absence of added HCl. In this reaction, however, 45.0 mmoles of starting hexafluorocyclobutene was mixed with 90.0 mmoles of aluminum chloride. After the initial separation, 44.5 mmoles (yield 99%) of hexachlorocyclobutene melting at $48-50^\circ$ was obtained. One recrystallization from methanol raised the melting point to $51-52^\circ$.

The reaction was carried out as before with the exception that 1,2-dichlorotetrafluorocyclobutene (Peninsular Chemical Research) was substituted for hexafluorocyclobutene. After the initial separation, the only product which was obtained was perchlorocyclobutene.

Hexabromocyclobutene.—Aluminum bromide (16 g) was added to a 100-ml Fisher-Porter glass pressure tube in a drybox. After helium leak checking, evacuating, and cooling the container (77°K), 3.24 g of hexafluorocyclobutene was condensed into the tube.

The mixture was slowly warmed to 0° whereupon the surface of the aluminum chloride was observed to undergo marked color changes. After standing for 16 hr, the mixture was washed with iced HCl and the aqueous layer extracted with chloroform.

Subsequent drying and evaporation of the organic layer provided 9.5 g (90%) of brown crystals (mp $142-146^\circ$). Two recrystallizations from absolute methanol gave cream platelets melting at $148-149.5^\circ$ (sealed tube). The Rast molecular weight was found to be 539 (calculated, 528). The infrared spectrum for this compound was extremely simple with bands at 1585 (C=C), 1150, 865, and 670 cm^{-1} .

Anal. Calcd for C_4Br_6 : C, 9.2; Br, 90.8. Found: C, 8.7; Br, 91.9.

An identical preparation starting with 1,2-dichlorotetrafluorocyclobutene also provided a good yield of hexabromocyclobutene. However, the reaction of hexachlorocyclobutene with AlBr_3 failed even at elevated temperatures.

(6) J. M. Howald, Ph.D. Thesis, Cornell University, 1953.

1,2-Dichlorohexafluorocyclopentene with Lewis Acids.—An excess of anhydrous aluminum chloride was added to the chloro-fluoroalkene at 0°. A brilliant green color developed on the surface of the AlCl₃ during the addition and remained during the 14-hr reaction time (temperature, 25°). The resulting mixture was extracted with CCl₄, washed, and dried over CaCl₂; the solvent was evaporated. A colorless oil remained which produced low-melting crystals upon treatment with anhydrous methanol. The infrared spectrum (major bands at 1610 (C=C), 1190, 1010, 1030, 905, 890, 865, 760, 685 cm⁻¹) was identical with that of an authentic sample of octachlorocyclopentene.

When AlBr₃ was substituted for AlCl₃ in the preceding experiment, cream colored platelets resulted. Recrystallization from absolute ethanol gave white rhombs, mp 123–124°. The infrared spectrum of the product was similar to octachlorocyclopentene, with absorption of 1610 (C=C), 1175, 1150, 885, 760, 740, and 675 cm⁻¹. The location of the C=C stretching frequency at 1610 cm⁻¹ suggests that the double bond still contains the original two chlorines.⁷

Anal. Calcd for C₅Br₂Cl₂: C, 9.83; Br, 78.7. Found: C, 10.07; Br, 78.2.

Reaction of Perfluorocyclohexene with AlCl₃ and AlBr₃.—The fluoro olefin was vacuum transferred onto excess aluminum chloride at -80° and the temperature was raised to 0°. After 30 min the mixture was warmed to 25° and allowed to react for 24 hr. The mixture was then extracted with CCl₄F and concentrated. The crude concentrate which crystallized as white needles was run through a gas chromatograph. Gas chromatography and infrared analysis indicated that only a single material had been formed. After recrystallization from isopropyl alcohol, infrared analysis and melting point established that the product was hexachlorobenzene.

Perfluorocyclohexene was treated with AlBr₃ in the same fashion as with AlCl₃. This reaction yielded four main products (all containing bromine). None of these materials has been completely characterized, and work is continuing with this reaction.

Reaction of *cis*- and *trans*-Perfluorobutene-2 with AlCl₃.—This reaction was attempted under a wide variety of conditions. Several products were usually obtained from this interaction—the relative ratios of these materials varied with the degree of severity of reaction. The starting material was 75% *trans*-perfluorobutene-2 containing 25% *cis* material in all cases. When perfluorobutene-2 with excess AlCl₃ was allowed to stand at room temperature for long periods, all of the starting fluoro olefin was recovered unchanged.

The reaction was carried out in the usual manner, *vide infra*, but at elevated temperature (sealed glass tube which was half immersed in an 80° bath for 16 hr). A number of components were obtained upon chromatography of the resultant methylene chloride extract.

Chromatography on 3/8 in. × 20 ft (Apiezon L, 40% on Anakrom ABS) using a 120-cc/min helium flow gave four frac-

(7) The infrared spectra of the five-numbered cycles, octachlorocyclopentene, hexachlorocyclopentadiene, and 1,2-dichlorohexafluorocyclopentene, have double bond stretching frequencies at 1610, 1611, and 1620 cm⁻¹, respectively.

tions. Fraction 1 had an infrared spectrum similar to that for a *cis* and *trans* mixture of CF₂CCl=CClCF₂.⁶ Separation of the *cis-trans* mixture was accomplished on a column of 30% halocarbon 1025 liquid on Chromosorb P. A 3/8 in. × 12 ft column at 70° was employed. These materials showed a mass spectrum with a parent peak at 232 (C₄Cl₂F₆⁺) with the proper isotopic intensities for a material containing only two chlorines. The boiling points, infrared spectra, and nmr spectra (*cis*-CF₂, 60.8 ppm; *trans*-CF₂, 64.1 ppm relative to CCl₄F) of the separated isomers were in accord with the literature.⁸ The reaction was repeated several times with the predominantly *trans* starting material (3:1). In each case the product *cis*-CF₂CCl=CCl-CF₂ predominated over the *trans* isomer in a ratio of 3:2.

Fraction 2 was demonstrated to contain CCl₃CClCClCF₃. The C=C absorption is found at 1540 cm⁻¹, and the -CF₃ unit at 1210 and 1240 cm⁻¹.⁹ The nmr spectra consisted of an unsplit signal at 74.8 ppm relative to CCl₄F. The mass spectrum contains a parent six peak cluster between 280 and 290 having the proper ratio for a compound containing five chlorine atoms. The mass spectral cracking pattern contains strong signals due to C₃Cl₅⁺, CCl₃⁺, and CF₃⁺. The material is a colorless liquid, bp 120° at 140 mm.

Anal. Calcd for C₄Cl₅F₂: C, 17.0; F, 20.2. Found: C, 16.8; F, 19.9.

Fraction 3 from this reaction was proved to be perchlorobutadiene. Infrared and mass spectra were identical with those of an authentic sample. Yields on a typical reaction were as follows: *trans*-CF₂CCl=CClCF₂, 2.7%; *cis*-CF₂CCl=CClCF₂, 8.1%; CF₂CCl=CClCCl₂, 61%; CCl₂=CClCCl₂=CCl₂, 28%.

Several experiments were carried out exactly as in the preceding reaction with the exception that the temperature was increased. For these experiments, the materials were treated at 110° for 18 hr. Separation of a methylene chloride extract by distillation and gas chromatography normally indicated the presence of four products. Separation on a spinning-band column gave the materials in order of their increasing boiling points. These were 1,1,1-trifluoropentachlorobutene-2 hexachloroethane, hexachlorobutadiene, and hexachlorobenzene (pot residue from vacuum distillation). 1,1,1-Trifluoropentachlorobutene and hexachlorobutadiene were minor components from this reaction, while the other two constituents were the major components being present in approximately equal quantities. Both hexachloroethane (mp 183–185°) and hexachlorobenzene were identified from their crystalline forms, melting points, and infrared spectra. Carbon-chlorine analysis, X-ray powder pattern, and mass spectrum of the crystals melting at 183–185° were consistent with those of hexachloroethane.

Acknowledgment.—We are indebted to Dr. L. P. Quinn of this laboratory for several discussions of this work. We also thank Mr. B. B. Goshgarian for furnishing mass spectral data.

(8) F. Dickinson, K. Hill, and J. Muray, *J. Chem. Soc.*, 1441 (1958).

(9) Reference 6 contains C=C stretching frequency for a number of similar compounds. Thus, CCl₃CCl=CClCCl₂ has a band at 1535 cm⁻¹, CCl₂-CCl=CCl₂, at 1550 cm⁻¹, and CF₂CCl=CCl₂ at 1575 cm⁻¹.