5.00 g (0.0335 mol) of propionanilide and 12.96 g (0.0336 mol) of 1 was heated for 24 hr in an oil bath maintained at 200°. At the conclusion of this period, there was no evidence of bismuth metal in the reaction mixture. The mixture was allowed to cool, and was then extracted with three 50-ml portions of chloroform. The organic extracts were filtered, combined, washed with saturated aqueous $NaHCO_3$, and concentrated to afford a black, oily residue (4.99 g).

This residue was dissolved in hot carbon tetrachloride. Cooling of this solution afforded a brown, flocculent precipitate (1.52 g) which was filtered from the mother liquors. This brown solid was then extracted with hot hexane; the solution, on cooling, deposited whitish crystals (A), weight 0.41 g. The mother liquors obtained from filtration of the flocculent precipitate were concentrated, yielding, on cooling, a black, crystalline mass. Several recrystallizations of this mass from hexane afforded two additional crops of off-white crystals B, 1.65 g, and C, 0.33 g.

Solids A, B and C all exhibited melting points with a wide range in the area between 79 and 95°, and nmr ($CDCl_3$) of all three contained the same general features: δ 8.2 (s, NH), 7.35 (m, ArH), 2.33 (q, J = 7 Hz, CH_3CH_2CO– of propionanilide), 2.10 (s, CH_3CO– of acetanilide), and 1.17 (t, J = 7 Hz, CH_3-CH_2CO– of propionanilide). All of these peaks with these characteristics were observed in the nmr of pure acetanilide and/or propionanilide. Ratios of the integration of the area under the peak at 2.10 to that under the peak at 1.17 were found to be 40:60, 49:51, and 50:50 for A, B, and C, respectively. Since these areas should be proportionate measures of the population of each of the two amides, it seems clear that about half of the propionanilide was converted to acetanilide.

Reaction of 1 with Amines. Representative Procedure (Aniline).—A mixture of 1.18 g (0.0127 mol) of aniline and 3.94 g (0.0102 mol) of 1 was heated at 150° for 3 hr. The mixture was allowed to cool and was then extracted with three 30-ml portions of chloroform. These extracts were filtered and concentrated to afford a white, crystalline residue, yield after drying, 1.46 g (86%), mp 113.5–115° (reported[13] for acetanilide, mp 113.9–114.4°). An ir spectrum ($CHCl_3$) of the product was identical with that of authentic acetanilide. The inorganic solid remaining after initial extraction of the reaction mixture with chloroform was filtered and pressed dry. Its ir spectrum[11] was essentially the same as that of bismuthyl acetate, $Bi(O)OCOCH_3$, described earlier.

For more reactive amines, it was necessary to carry out the reaction at lower temperatures in a nitrogen atmosphere; thus, reaction of *p*-anisidine at 105° for 24 hr under nitrogen afforded a 34% yield of recrystallized *N*-acetyl-*p*-anisidine, mp 127–128.5°, undepressed on admixture with an authentic sample, ir ($CHCl_3$) identical with that of authentic *p*-acetanisidide.

Reaction of 1 with Hydrazobenzene.—A mixture of 0.421 g (2.29 mmol) of hydrazobenzene and 1.09 g (2.84 mmol) of 1 was heated at 130° under nitrogen for 3 hr. The mixture was then allowed to cool and was extracted with three 30-ml portions of chloroform. The organic extracts were filtered, combined, and concentrated, affording an orange, crystalline residue. Recrystallization of the solid product from an ethanol–water mixture afforded orange crystals (0.220 g, 53%) of azobenzene: mp 68–70°, undepressed on admixture with an authentic sample; ir ($CHCl_3$) identical with that of authentic azobenzene.

Reaction of 1 with Alcohols. Representative Procedure (Dodecanol).—A mixture of 2.10 g (0.0113 mol) of dodecanol and 4.82 g (0.0124 mol) of 1 was heated at 150° for 24 hr. After the mixture was allowed to cool, it was extracted with three 30-ml portions of methylene chloride. The residual inorganic solid was rinsed with methylene chloride and pressed dry; its ir spectrum[11] identified it as bismuthyl acetate. The organic extracts were washed with saturated aqueous $NaHCO_3$, concentrated, and distilled to afford 1.53 g (60%) of a clear, colorless liquid: bp 94° (0.30 mm) [reported[16] bp 139–140° (9 mm)]; ir ($CHCl_3$) 1750 (ester C=O), 1370 cm^{-1} (CH_3C).

Reaction of 1 with Formates. Representative Procedure (Cholesteryl Formate).—A mixture of 4.87 g (0.0126 mol) of 1 and 5.18 g (0.0125 mol) of cholesteryl formate was heated at 190° for 48 hr. After the reaction mixture was allowed to cool, the resultant mixture of bismuth metal and brown solid was extracted with three 30-ml portions of methylene chloride. The organic extracts were dried ($MgSO_4$) and concentrated to yield 5.05 g of a brown solid. This was recrystallized from 95% ethanol to afford 4.68 g (87%) of yellow-white crystals: mp 112–113.5° (reported[17] mp 114°); ir ($CHCl_3$) (identical with that of the product isolated from reaction of cholesterol with 1) exhibits increases in absorption at 1025, 1190–1250, and 1370 cm^{-1} compared with the spectrum of the starting formate; nmr (CCl_4) δ 1.94 (s, CH_3CO–). The addition of a small amount of benzoyl peroxide to a parallel reaction under conditions similar to these appeared to have no measurable effect on either the course or speed of the reaction.

Registry No.—1, 22306-37-2.

Acknowledgment.—The financial support of the National Science Foundation Undergraduate Research Participation Program for this work is gratefully acknowledged.

[16] M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **27**, 950 (1944).

[17] A. H. Milburn and E. V. Truter, *J. Chem. Soc.*, 1736 (1956).

Fluorinated Cyclopropenes and Cyclopropenium Ions[1]

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Tetrachlorocyclopropene (1) was fluorinated with potassium fluoride in tetramethylenesulfone at 160–180° to give 1,2,3-trichloro-3-fluorocyclopropene (2), 1,2-dichloro-3,3-difluorocyclopropene (3), 1-chloro-2,3,3-trifluorocyclopropene (4), plus two ring-opened products, the pentafluoropropene 5 and the pentafluoropropane 6. Tetrabromocyclopropene (7) was fluorinated under similar conditions to give 1,2-dibromo-3,3-difluorocyclopropene (8), 1-bromo-2,3,3-trifluorocyclopropene (9), 5, and 6. The fluorocyclopropenes 3, 4, 5, and 6 reacted with antimony pentafluoride to give the fluorocyclopropenium hexafluoroantimonates, 15, 16, 17, and 18, respectively. The physical properties of the compounds herein described are compared with those of analogous, known species. A mechanism for the fluorination of 1 and 7 by potassium fluoride is proposed.

The Preparation of Fluorocyclopropenes.—Tetrachloro- and tetrabromocyclopropenes **1** and **7** undergo halogen exchange readily in the presence of Lewis acids through the intermediacy of the corresponding trihalocyclopropenium ions, which have been isolated and studied in some detail.[2] Thus tetrachlorocyclopropene (**1**) reacts with an excess of boron tribromide to give tetrabromocyclopropene (**7**).[3] Both **1** and **7** can be fluorinated at the allylic position by antimony trifluoride to give 1,2,3-trichloro-3-fluorocyclopropene

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[1] Taken in part from the Ph.D. thesis of D. C. F. Law, University of Wisconsin, 1967, also presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract of Papers, S52.

[2] R. West, A. Sadô, and S. W. Tobey, *J. Amer. Chem. Soc.*, **88**, 2488 (1966).

[3] S. W. Tobey and R. West, *ibid.*, **88**, 2481 (1966).

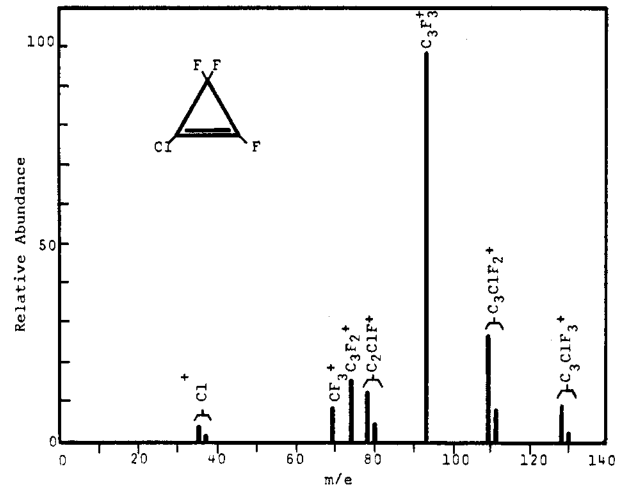
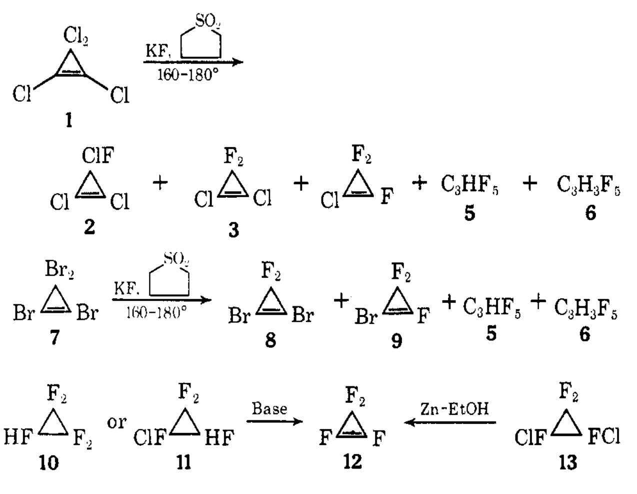


Figure 1.—Mass spectrum of 1-chloro-2,3,3-trifluorocyclopropene (4).

(2), 1,2-dichloro-3,3-difluorocyclopropene (3), and 1,2-dibromo-3,3-difluorocyclopropene (8), respectively.[3]

Since the fluorination of 1 and 7 by antimony trifluoride effects halogen exchange at the allylic position only without affecting the vinylic halogens, we decided to investigate the same reaction using a nucleophilic fluorinating reagent. With potassium fluoride in tetramethylenesulfone at 180°, fluorination of 1 and 7 occurred not only at the allylic position, but also at one of the vinylic positions. Thus tetrachlorocyclopropene (1) reacted to yield 2, 3, 1-chloro-2,3,3-trifluorocyclopropene (4), and two ring-opened products, the pentafluoropropene 5 and the pentafluoropropane 6 (the last two compounds have not been completely characterized). Under similar conditions, tetrabromocyclopropene (7) was fluorinated by potassium fluoride to give 1,2-dibromo-3,3-difluorocyclopropene (8), 1-bromo-2,3,3-trifluorocyclopropene (9), 5, and 6.

After this work was completed, Sargeant and Krespan reported that tetrafluorocyclopropene (12) was prepared by the dehydrohalogenation of pentafluorocyclopropane (10) or 1-chloro-1,2,2,3-tetrafluorocyclopropane (11), and most conveniently by the dechlorination of 1,2-dichloro-1,2,3,3-tetrafluorocyclopropane (13).[4]



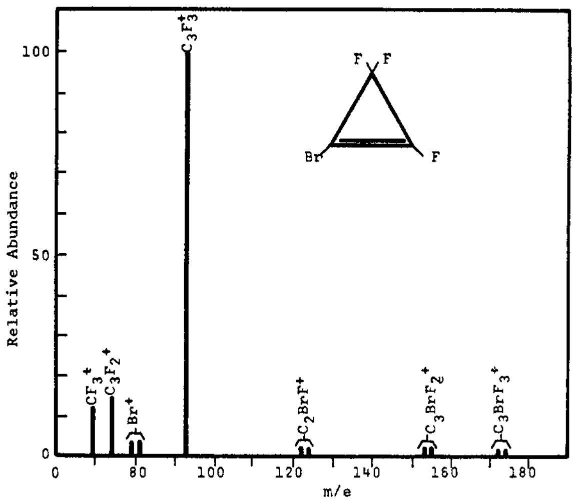


Figure 2.—Mass spectrum of 1-bromo-2,3,3-trifluorocyclopropene (9).

Therefore, except for the iodocyclopropenes, which are expected to be very unstable,[5] most of the perhalocyclopropenes have now been prepared and characterized.

The Properties of Fluorocyclopropenes.—1,2,3-Trichloro-3-fluorocyclopropene (2), bp 96°, 1,2-dichloro-3,3-difluorocyclopropene (3), bp 58°, and 1,2-dibromo-3,3-difluorocyclopropene (8), bp 105°, were identified by their boiling points, ir, and ^{19}F nmr data, which are identical with those of the authentic samples previously reported.[3] The structural assignments of 1-chloro-2,3,3-trifluorocyclopropene (4), bp 28°, and 1-bromo-2,3,3-trifluorocyclopropene (9), bp 38°, are based on evidence described below.

The mass spectra of 4 and 9 are shown in Figures 1 and 2, respectively. The fragmentation patterns of 4 and 9 are very similar except that species containing a chlorine are relatively more abundant than those containing a bromine. Both 4 and 9 give base peaks corresponding to the rearrangement ion, $C_3F_3^+$ (*m/e* 93), and molecular ions corresponding to $C_3ClF_3^+$ (*m/e* 128) and $C_3BrF_3^+$ (*m/e* 172, 174), respectively.

The infrared spectra of 4 and 9 are strikingly similar (see Experimental Section). The bands at 1860 and 1850 cm^{-1} shown by 4 and 9, respectively, can be attributed to the C=C stretching vibration and may be compared to the corresponding ir active bands found for other cyclopropenes (Table I). Among the perhalocyclopropenes, hypsochromic shifts of the C=C stretching frequency accompany a decrease in the mass

Table I

Carbon–Carbon Double Bond Stretching Vibration Frequencies of Cyclopropenes

Cyclopropene	$\nu_{C=C}$, cm^{-1}
C_3H_4	1641[a]
C_3Br_4 (7)	1757
C_3Cl_4 (1)	1810
C_3Cl_3F (2)	1820
C_3BrF_3 (9)	1850
C_3ClF_3 (4)	1860
C_3F_4 (12)	1945[b]

[a] Reference 6. [b] Reference 4.

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[4] P. B. Sargeant and C. G. Krespan, *J. Amer. Chem. Soc.*, **91**, 415 (1969).

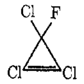
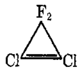
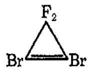
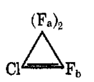
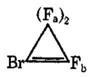
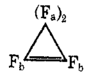
[5] An unsuccessful attempt to prepare 1,2-diiodo-3,3-dichlorocyclopropene was reported by H. M. Cohen and A. H. Keough, *J. Org. Chem.*, **31**, 3428 (1966).

of the halogen substituents. A parallel mass effect is also observed in some vibrational frequencies of the perhalocyclopropenium ions (see Table IV).

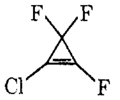
The ^{19}F nmr data of the fluorocyclopropenes are summarized in Table II. The ^{19}F nmr spectrum of **4** is consistent with the structure of 1-chloro-2,3,3-trifluorocyclopropene, but excludes the alternative isomeric structure, 3-chloro-1,2,3-trifluorocyclopropene (**14**). The two allylic fluorines of **4** appear as a doublet

TABLE II

^{19}F NMR DATA FOR FLUOROCYCLOPROPENES

Cyclopropene	Chemical shift, ppm	J_{F-F}, cps	$J_{^{13}C-F}$, cps
 **2**	99.8		
 **3**	99.8		292
 **8**	98.1		320 ± 5
 **4**	(a) 98.5 (doublet) (b) 127.8 (triplet)	41.4	(a) 292.8 (b) 445.2
 **9**	(a) 97.2 (doublet) (b) 124.2 (triplet)	41.1	(a) 292.9 (b) 444.5
 **12**	(a) 96.7 (triplet)[a] (b) 145.1 (triplet)	43.5	

[a] Reference 4.



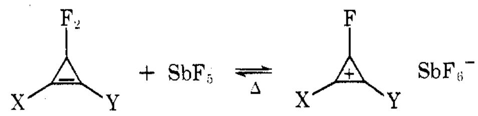
14

(J_{F-F} = 41.4 cps) at 98.5 ppm, which is consistent with the chemical shifts of allylic fluorines in other fluorocyclopropenes (see Table II). The vinylic fluorine of **4** appears as a triplet at 127.8 ppm. The unknown isomer **14** would be expected to show a doublet for the vinylic fluorines at *ca.* 145 ppm, and a triplet for the allylic fluorine at *ca.* 99 ppm. Furthermore, the pattern of the satellites due to $^{13}C-^{19}F$ couplings in the spectrum of **4** provides definitive proof of the assigned structure, as they consist of a pair of doublets about the main doublet ($J_{^{13}C-F}$ = 292.8 cps) and a pair of triplets about the main triplet ($J_{^{13}C-F}$ = 445.2 cps). In the case of structure **14**, the satellites of the main doublet would be expected to appear as a pair of quartets owing to the nonequivalence of the vinylic fluorines in the ^{13}C-labeled species. The structure of **9** can also be unambiguously assigned on similar ^{19}F nmr evidence (see Table II). The $^{13}C-^{19}F$ and $^{13}C-^{12}C-^{19}F$ spin–spin couplings in fluorocyclopropenes are relatively insensitive to the variation of halogen substituents on the ring, as shown by the data in Table III.

Diels–Alder reactions of all the perhalocyclopropenes mentioned above have already been reported.[6,7] It is interesting to note that the relative rate-enhancing effect of halogen substituents on the cyclopropene's dienophilic reactivity toward furan is Br > Cl > F. This trend is consistent with the observation that small ring systems are stabilized by fluorine substitution relative to chlorine substitution.[7]

Fluorocyclopropenium Ions.—Cyclopropenium ions are now well known as stable aromatic species with two π electrons, and a variety of more or less stable salts of substituted cyclopropenium ions have been prepared,[8] including some perhalocyclopropenium salts.[3,4]

When the fluorocyclopropenes **3**, **4**, **8**, and **9** were treated with antimony pentafluoride, an allylic fluorine was removed from the cyclopropene and the corresponding trihalocyclopropenium hexafluoroantimonates, **15**, **16**, **17**, and **18**, could be isolated. These complexes are the first examples of stable, unsolvated fluorocarbonium ion salts. Sargeant and Krespan also reported that **12** reacted with antimony pentafluoride to give the complex **19** in antimony pentafluoride solution.[4]



3, X = Y = Cl	**15**, X = Y = Cl
4, X = Cl; Y = F	**16**, X = Cl; Y = F
8, X = Y = Br	**17**, X = Y = Br
9, X = Br; Y = F	**18**, X = Br; Y = F
12, X = Y = F	**19**, X = Y = F

That the integrity of the three-member ring is preserved in these complexes is proved by the observation that upon gentle heating, the original tetrahalocyclopropenes could be regenerated from the corresponding complexes. Further proof is provided by ir, ^{19}F nmr, and chemical evidence (*vide infra*).

The infrared spectra of the cyclopropenium ion salts are listed in the Experimental Section. The solvent, antimony pentafluoride, has no absorptions between 4000 and 800 cm^{-1} but absorbs strongly below 750 cm^{-1}. In each spectrum, bands due to the parent cyclopropenes are entirely absent. The infrared spectra of **15** and **17**, and of **16** and **18**, are very similar, indicating that the infrared absorption is due principally to C–C and C–F modes. Frequencies of the two vibrational fundamentals characteristic of perhalocyclopropenium ions are listed in Table IV. For trichlorocyclopropenium ion, the band at 1791 cm^{-1} is the totally symmetric ring stretching mode, of class A, inactive in the infrared but observed in the Raman spectrum.[2] The lowered symmetry of the partly fluorinated cyclopropenium ions allows observation of the corresponding band in the infrared. The lower frequency band, at 1312 cm^{-1} in $C_3Cl_3^+$, is assigned to a mode involving mostly ring expansion and compression.[2] Both bands shift somewhat to higher frequencies as the heavier halogens are replaced by fluorine.

The ^{19}F nmr data for the fluorocyclopropenium ions in either SO_2 or SO_2–SbF_5 solutions are summarized in Table V. In all cases, a singlet between 62.0 and 63.6 ppm (referenced to external trichlorofluoro-

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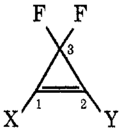
[6] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1266 (1961).

[7] D. C. F. Law and S. W. Tobey, *ibid.*, **90**, 2376 (1968).

[8] For a review of cyclopropenium ion chemistry, see A. W. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965).

TABLE III
^{13}C–F AND ^{13}C–C–F COUPLINGS IN FLUORINATED TETRAHALOCYCLOPROPENES



		C₃–F		C₂–F		C₁–C₃–F		C₁–C₂–F		C₂–C₃–F		C₃–C₂–F
X	Y	J, cps	I.S.,[a] ppm	J, cps	I.S., ppm	J, cps	I.S., ppm	J, cps	I.S., ppm	J, cps	I.S., ppm	J, cps[b]
Cl	F	292.8	0.123	445.2	0.116	20.6	0.023	20.6	0.051	15.3	0.028	7.5
Cl	Cl	293.3	0.123			17.5	0.025			17.5	0.025	
Br	F	293.0	0.123	444.6	0.117	21.4	0.021	17.8	0.049	14.9	0.028	7.7
Br	Br	320 ± 5										

[a] I.S. = isotopic shift. [b] Maximum possible, $J = 10.5$ cps; minimum possible, $J = 4.5$ cps.

TABLE IV
CHARACTERISTIC VIBRATIONAL FREQUENCIES OF TRIHALOCYCLOPROPENIUM IONS

Cyclopropenium ion	Band 1, cm⁻¹	Band 2, cm⁻¹
$C_3Cl_3^+$	1791[a]	1312[a]
$C_3Cl_2F^+$ (15)	1880	1400 (broad)
$C_3ClF_2^+$ (16)	1960	1450
$C_3Br_3^+$		1276[a]
$C_3Br_2F^+$ (17)	1870	1390, 1370 (doublet)
C_3BrF_2 (18)	1940	1420

[a] Reference 2.

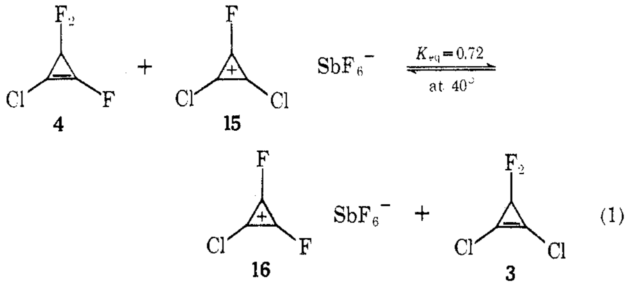
TABLE V
^{19}F NMR DATA OF FLUORINATED TRIHALOCYCLOPROPENIUM IONS

Cyclopropenium ion	Chemical shift, ppm
$C_3Cl_2F^+$ (15)	63.39
$C_3ClF_2^+$ (16)	63.58[a]
$C_3Br_2F^+$ (17)	62.0
$C_3BrF_2^+$ (18)	62.6
$C_3F_3^+$ (19)	63.1[b]

[a] $J_{^{13}C-F} = 458$ cps; $J_{F-F} = 3.5$ cps. [b] Reference 4.

methane) was observed which does not change significantly in the temperature range −70 to 40°. For example, $C_3ClF_2^+SbF_6^-$ (16), dissolved in SO_2, shows a singlet at 63.58 ppm which is due to the two equivalent fluorines in $C_3ClF_2^+$, and a pair of satellites about the main singlet ($J_{^{13}C-F} = 458$ cps). Each of the satellites consists of a doublet due to spin–spin coupling of adjacent fluorines ($J_{F-F} = 3.5$ cps). The observation of ^{13}C–F spin–spin coupling at room temperature is conclusive evidence that the spectrum is due to the fluorocyclopropenium ion alone and that fluorine exchange between the latter and SbF_6^- is slow relative to the nmr time scale.[9] We failed to observe a signal due to SbF_6^-, probably because of rapid fluorine exchange between the latter and a certain amount of SbF_5 present in the sample, with resultant broadening of the fluorine resonance signal.[10]

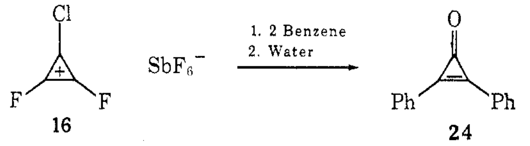
When a mixture of 1-chloro-2,3,3-trifluorocyclopropene (4) and 1,2-dichloro-3-fluorocyclopropenium hexafluoroantimonate (15) was dissolved in SO_2 in a sealed tube, an equilibrium mixture of 4, 15, 16, and 3 was established rapidly and the ^{19}F nmr spectrum due to each species was observed individually, indicating that fluorine exchange between the fluorocyclopropenes and the fluorocyclopropenium ions is also slow relative to the nmr time scale. The equilibrium constant, K_{eq}, for the following reaction (eq 1) was determined



by the integrated nmr spectral intensities to be 0.72 at 40°.

The ^{19}F nmr signal of the fluorines in the fluorocyclopropenium ions is shifted downfield by 35 ± 1 ppm from the allylic fluorines and by 61–82 ppm from the vinylic fluorines in the corresponding fluorocyclopropenes (*cf.* Table II and Table IV). These downfield shifts are consistent with the deshielding effect observed in other fluorocarbonium ions such as difluorophenyl- and fluorodiphenylcarbonium ions.[11]

1-Chloro-2,3-difluorocyclopropenium hexafluoroantimonate (16) underwent Friedel–Craft reaction with an excess of benzene followed by hydrolysis to give diphenylcyclopropenone (24).[12] Similar reactions of



trichloro- and tribromocyclopropenium ions with aromatic compounds have been reported.[13]

Discussion

The halogen substituents on the perhalocyclopropenes are either allylic or vinylic. Under the conditions used in our investigation, the displacement of the allylic halogens (from here on, the term halogen refers to chlorine or bromine as distinguished from fluorine) by fluoride ions could conceivably arise *via* SN1, SN2, SN2′, or a carbanion mechanism analogous to a nonconcerted "SN2′" reaction. However, an SN2 mech-

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[9] N. S. Ham, E. A. Jeffery, T. Mole, and S. N. Stuart, *Chem. Commun.*, 254 (1967).

[10] Sargeant and Krespan also failed to observe a signal due to SbF_6^-; see ref 4.

[11] G. A. Olah, C. A. Cupas, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 362 (1966).

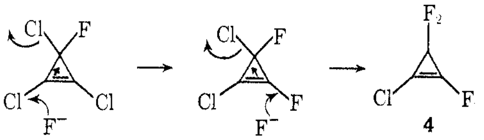
[12] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson and J. Posner, *ibid.*, **87**, 1320 (1965).

[13] (a) R. West, D. Zecher, and W. Goyert, *ibid.*, **92**, 149 (1970); (b) R. West, D. Zecher, and S. W. Tobey, *ibid.*, **92**, 168 (1970).

anism is highly unlikely because of the excessive steric strain that would develop in the transition state involving a three-membered ring.[14] On the other hand, there is indirect evidence to suggest that the SN1, SN2′, or carbanion mechanisms might play a role either individually or collectively.

The SN1 pathway would involve the initial ionization of an allylic halogen to form an aromatic trihalocyclopropenium ion, the stability of which has been demonstrated (*vide supra*). The observation that the hydrolysis of **1** in 75% dioxane–25% water in the presence of excess hydroxide ion followed first-order kinetics[15] also lends support to the SN1 mechanism in the fluorination of **1** or **7** by potassium fluoride in the strongly polar solvent tetramethylenesulfone.

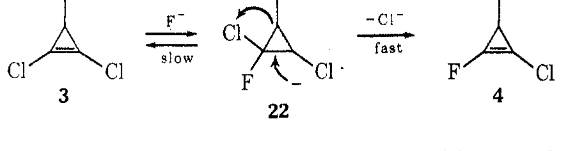
At present, no data are available for our system or analogous systems to distinguish between a truly concerted SN2′ mechanism and an analogous, nonconcerted mechanism involving a carbanion intermediate. Either of these mechanisms might be involved, since it is well known that nucleophilic attack of perhalocycloalkenes (having four, five, and six carbons) by alkoxide ions may result in displacement with rearrangement of the double bond.[16–18] Such reactions could lead to a hitherto unobserved product **23** through



2 **23** **4**

the attack of **2** by fluoride. The absence of **23** can be explained by the extreme susceptibility of a fluorine-carrying trigonal carbon toward nucleophilic attack.[17] Thus any **23** formed would be expected to react rapidly with fluoride to give **4**. The latter, though possessing also a fluorine-carrying trigonal carbon, should be less reactive than **23** toward fluoride because it has no labile halogen to be displaced (*vide infra*) and is therefore isolable.

The displacement of a vinylic halogen in a perhalocyclopropene by a fluoride ion could arise through the initial addition of the fluoride to the double bond to form a carbanion intermediate, followed by the elimination of a halide ion from an adjacent carbon, as for example in the sequence **3**, **22**, and **4**. A similar mechanism has



3 **22** **4**

been postulated to explain the nucleophilic attack of perhalocycloalkenes (having four, five and six carbons) by alkoxide ions.[16–18]

On the basis of exchange reactions of various "haloforms,"[19] the stabilization of carbanions by α substituents is in the order I $\sim$ Br > Cl > F > OEt while nmr studies[20] have established the following order of "apparent electron-withdrawing power" for α substituents: I > Br > Cl > F $\gg$ CF_2Br > CF_2Cl > CF_3. The attack on **4** or **9** by fluoride would necessarily be directed exclusively at the fluorine-carrying trigonal carbon because the developing negative charge could be stabilized by the chlorine or bromine at the adjacent carbon. The fate of the resulting carbanions, which have no labile leaving group for elimination, is apparently ring opening, leading eventually to **5** and **6**.

In contrast, chlorinated cyclopentenes and cyclohexenes, which have no tendency to ring open, can undergo relatively facile and complete fluorination by potassium fluoride. Maynard reported that, under conditions similar to ours, perchlorocyclopentene (**26**) was completely fluorinated to give perfluorocyclopentene (**27**) in *ca.* 74% yield, while 1,2-dichloro-3,3,4,4,5,5,6,6-octafluorocyclohexene (**28**) gave perfluorocyclohexene (**29**) in 71% yield.[21] As the steric strain of the cyclic compounds increases by the introduction of more double bonds, fluorination apparently becomes more difficult and less complete. Thus 1,2,4,5-tetrachloro-3,3,6,6-tetrafluoro-1,4-cyclohexadiene (**30**) reacted with potassium fluoride to give a mixture of perfluoro-1,4-cyclohexadiene (**31**) (10% yield) and 1-chloro-2,3,3,4,5,5,6,6-heptafluoro-1,4-cyclohexadiene (**32**) (10% yield), whereas perchlorocyclopentadiene (**33**) gave only intractable resinous products.[21]

Experimental Section

Materials.—Tetrachlorocyclopropene (1) and tetrabromocyclopropene (7) were prepared by the method of Tobey and West.[2] Tetramethylenesulfone was obtained from Eastman Organic Chemicals and was dried over calcium hydride and distilled under vacuum before use. Anhydrous potassium fluoride was obtained from Allied Chemical and dried by heating at 150° under vacuum for 4 hr before use. Antimony pentafluoride was obtained from Allied Chemical Corp. and distilled under a nitrogen atmosphere (bp 140°, lit. bp 149.5°) before use. Anhydrous sulfur dioxide was obtained from Matheson Chemical Co. and used directly from the cylinder.

Instrumentation.—Infrared spectra were obtained on a Perkin-Elmer 237 spectrophotometer. The fluorocyclopropenes were sampled in a 10-cm gas cell equipped with sodium chloride windows at a pressure of about 4 Torr. The ir spectra of the fluorocyclopropenium hexafluoroantimonates were taken as solutions in antimony pentafluoride as a film between Irtran 2 (zinc sulfide) plates. Mass spectra were determined on a CEC 21-110 spectrometer. ^{19}F nmr spectra were obtained on a Varian A56-60 spectrometer at 56.4 MHz. All chemical shifts are referenced to external trichlorofluoromethane. Some of the ^{13}C–^{19}F spin-spin coupling data were obtained on a Varian HA-100 nmr spectrometer at 94.1 MHz. Gas chromatographic separations employed a 20 ft × 0.25 in. stainless steel column packed with 30% dinonyl phthalate on 45–60 mesh Chromosorb W.

The Fluorination of Tetrachlorocyclopropene (1).—Anhydrous potassium fluoride (63.6 g, 1.1 mol) and dry tetramethylenesulfone (130 ml) were placed in a 500-ml three-necked flask equipped with a Teflon blade stirrer, an addition funnel, and an air-cooled reflux condenser, the outlet of which was connected to a series of two cold traps immersed in solid carbon dioxide–acetone and liquid nitrogen, respectively. The flask was half immersed

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[14] E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 122.

[15] S. W. Tobey and A. M. McGinnis, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, Abstracts of Papers, 0-153.

[16] J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, **31**, 1117 (1966).

[17] J. D. Park, R. J. McMurtry, and R. Sullivan, *ibid.*, **33**, 33 (1968).

[18] A. B. Clayton, J. Roylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 7358 (1965).

[19] (a) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 1406 (1957); (b) J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *ibid.*, **83**, 1219 (1962); (c) L. H. Slaugh and E. Bergman, *J. Org. Chem.*, **26**, 3158 (1961).

[20] G. V. D. Tiers, *J. Amer. Chem. Soc.*, **78**, 2914 (1956).

[21] J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963).

in an oil bath which was maintained at 160–180°, while a slow stream of dry nitrogen was passed into the addition funnel, through the flask, the condenser, the cold traps, and out of a bubble counter filled with mineral oil. A solution of tetrachlorocyclopropene (**1**) (33.4 g, 0.188 mol) in 20 ml of tetramethylenesulfone was slowly added from the addition funnel into the flask with vigorous stirring over a period of 5 hr. About 5 ml of liquid product was collected in the cold traps and subsequently fractionated through a 10-cm Vigreux column. As the crude product warmed to room temperature, a gaseous distillate was collected in a Dry Ice trap and subsequently analyzed by gas chromatography. The following liquids boiling above room temperature were obtained by distillation.

1-Chloro-2,3,3-trifluorocyclopropene (**4**) had bp 28° (2 g, 7%); mol wt 128 (mass spectrum); ir (gas) 1860 (m), 1360 (s), 1290 (m), 1210 (s), 1120 (s), 880 (m), and 840 cm^{-1} (m); ^{19}F nmr, a doublet at 98.5 (2 F) and a triplet at 127.8 ppm (1 F), J_{F-F} = 41.4 cps.

1,2-Dichloro-3,3-difluorocyclopropene (**3**) had bp 58° (2.5 g, 8%); ir (gas) 1330 (s), 1300 (w), 1130 (w), 1100 (s), 850 (m), and 760 cm^{-1} (m); ^{19}F nmr, a singlet at 99.8 ppm.

1,2,3-Trichloro-3-fluorocyclopropene (**2**) had bp 96° (2.5 g, 7%); ir (liquid film) 1820 (w), 1270 (w), 1270 (w), 1240 (m), 1150 (w), 1095 (s), 1070 (w), 960 (s), 760 (w), and 700 cm^{-1} (s); ^{19}F nmr, a singlet at 99.8 ppm.

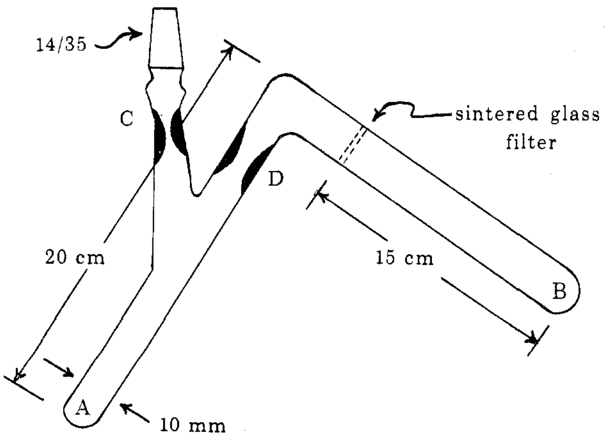
Two gaseous products were isolated by glc: the pentafluoropropene **5**, mol wt 132 (mass spectrum), ir (gas) 1760 (s), 1370 (s), 1330 (s), 1250 (w), 1170 (m), 1110 (s), 930 (s), and 890 cm^{-1} (w); and the pentafluoropropane **6**, mol wt 133 (mass spectrum), ir (gas) 1530 (w), 1410 (m), 1320 (m), 1250 (s), 1180 (w), 1120 (m), 970 (m), 920 (w), 840 (w), and 790 cm^{-1} (w).

The Fluorination of Tetrabromocyclopropene (7).—The apparatus and procedure are the same as described in the preceding section. A solution of tetrabromocyclopropene (**7**) in 20 ml of tetramethylenesulfone was slowly added with vigorous stirring to a mixture of anhydrous potassium fluoride (44.5 g, 0.768 mol) and 130 ml of tetramethylenesulfone at 160–180° under a nitrogen stream. About 5 ml of liquid product was collected in the cold traps. Separation by glc and distillation of the crude product gave, in addition to **5** and **6**, the following fluorocyclopropenes.

1-Bromo-2,3,3-trifluorocyclopropene (**9**) had bp 38° (1.55 g, 7%); mol wt 172, 174 (mass spectrum); ir (gas) 1850 (s), 1390 (w), 1365 (s), 1295 (m), 1275 (m), 1240 (w), 1200 (s), 1145 (m), 1115 (s), 880 (m), and 820 cm^{-1} (m); ^{19}F nmr, a doublet at 97.2 ppm (2 F) and a triplet at 124.2 ppm (1 F, J_{F-F} = 41.1 cps).

1,2-Dibromo-3,3-difluorocyclopropene (**8**) had bp 105° (2.1 g, 7%); ir (gas) 1325 (s), 1110 (s), 1090 (w), 835 (m), 820 (w), and 740 cm^{-1} (w); ^{19}F nmr, a singlet at 98.1 cps.

The Preparation of Fluorocyclopropenium Hexafluoroantimonates.—Analytically pure samples of the fluorocyclopropenium hexafluoroantimonates were prepared by means of the Pyrex device shown below.



One volume (*ca.* 0.5 ml) of freshly distilled antimony pentafluoride was placed in arm A of the device, which was then attached to a vacuum line through the 14/35 joint, and four volumes of a fluorocyclopropene and eight volumes of sulfur dioxide were successively condensed into arm A at liquid nitrogen temperature. The device was then sealed off under vacuum at the thickened part, C. The reaction mixture was allowed to warm up slowly and gently shaken, whereupon an exothermic reaction occurred and a pale yellow solution with a colorless layer of excess cyclopropene on top resulted. The device was then tilted so that the solution was allowed to filter through the sintered glass filter into arm B, which was cooled in liquid nitrogen. While the solution in arm B was warmed up to room temperature, sulfur dioxide and the excess cyclopropene were distilled back into arm A by immersing the latter in liquid nitrogen. When finally only a dry solid residue remained in arm B, the device was sealed off at the thickened part, D. Arm B, containing the fluorocyclopropenium hexafluoroantimonate complex, was broken open in a drybox filled with dry helium and the hygroscopic complex was handled in the absence of moisture. The following elemental analyses were obtained. *Anal.* Calcd for $C_3Cl_2F^+SbF_6^-$ (**15**): C, 9.96; Cl, 19.61; F, 36.77; Sb, 33.66. Found: C, 10.01; Cl, 19.30; F, 36.90; Sb, 33.54. Calcd for $C_3ClF_2^+SbF_6^-$ (**16**): C, 10.44; Cl, 10.27; F, 44.03; Sb, 35.27. Found: C, 10.31; Cl, 10.40; F, 44.51; Sb, 35.03. Clacd for $C_3Br_2F^+SbF_6^-$ (**17**): C, 8.00; Br, 35.47; F, 29.51; Sb, 27.02. Found: C, 7.97; Br, 35.08; F, 30.07; Sb, 26.82. Calcd for $C_3BrF_2^+SbF_6^-$ (**18**): C, 9.25; Br, 20.51; F, 39.00; Sb, 31.24. Found: C, 9.16; Br, 20.51; F, 39.40; Sb, 31.20.

The ^{19}F nmr samples of **15–18** were prepared as sulfur dioxide solutions in sample tubes sealed under vacuum while the samples were frozen under liquid nitrogen. A capillary containing trichlorofluoromethane placed inside the sample tube served as the external standard.

The ir spectra of **15–18** taken in SbF_5 solutions as a film between Irtran 2 plates are as follows. $C_3Cl_2F^+$ SbF_6^- (**15**): 1880 (s), 1830 (w), 1750 (w), 1660 (w), 1620 (w), 1550 (w), 1410 (s), 1150 (w), 940 (m) and 890 cm^{-1} (m). $C_3ClF_2^+SbF_6^-$ (**16**): 1960 (s), 1930 (w), 1900 (w), 1620 (s), 1590 (w), 1550 (s), 1500 (w), 1450 (s), 1410 (w), 1380 (w), 1280 (w), 1260 (w), 970 (m) and 920 cm^{-1} (m). $C_3Br_2F^+SbF_6^-$ (**17**): 1870 (s), 1780 (w), 1550 (w), 1440 (w), 1390, 1370 (s, doublet), 1260 (w), and 910 cm^{-1} (m). $C_3BrF_2^+SbF_6^-$ (**18**): 1930 (s), 1900 (w), 1870 (w), 1830 (w), 1610 (s), 1570 (w), 1520 (s), 1490 (w), 1450 (w), 1420 (s), 1300 (w), 1280 (w), 1260 (m), 1240 (w), 1140 (w), 1040 (w), 970 (m), 930 (w), and 900 cm^{-1} (s).

The Regeneration of Tetrahalocyclopropenes from Trihalocyclopropenium Hexafluoroantimonates.—A microspatula of $C_3Cl_2F^+SbF_6^-$ (**15**) was placed in a Pyrex tube attached to a vacuum line. The whole system was evacuated and closed. A thermometer was hung beside the sample, which was heated to *ca.* 80° by means of a hot air blower. The sample darkened and liquefied, and the pressure in the closed system rose to 30 Torr. An infrared spectrum of the collected gaseous product was identical with that of 1,2-dichloro-3,3-difluorocyclopropene (**3**).

The Preparation of Diphenylcyclopropenone (24) from 16.—One gram of $C_3ClF_2^+SbF_6^-$ (**16**) was added to 5 ml of benzene in a test tube, which was then loosely stoppered with a cork. The mixture was stirred and gently heated for 15 min, during which time a gas evolved. After the mixture was cooled to room temperature, cold water (10 ml) and solid sodium carbonate were successively added to neutralize the acidic mixture, which was then extracted with ether. The ether extract was dried over calcium chloride and evaporated to give a solid residue. The latter was then recrystallized from cyclohexane to give colorless diphenylcyclopropenone (**24**), mp 121–121.5° (lit. mp 121.5–122°), which had ir and uv spectra identical with those of an authentic sample.[12]

Registry No.—**1**, 6262-42-6; **2**, 6262-44-8; **3**, 6262-45-9; **4**, 24921-89-9; **5**, 37145-46-3; **6**, 37145-47-5; **7**, 6262-43-7; **8**, 6262-46-0; **9**, 29777-44-4; **15**, 37145-74-7; **16**, 37396-42-2; **17**, 37396-43-3; **18**, 37145-73-6.

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