nmr spectrum of **4** shows a sharp singlet resonance at τ 76.2 ($(-OCH_3)_2$); a doublet at 5.20 J = 1.2 cps ($-CH(OR)_2$); and a doublet at τ 3.31, J = 1.2 cps ($C{=}C{-}H$). The peak area ratios are 6:0.9:1.

Anal. Calcd for $C_5H_8Cl_2O_2$: C, 35.12; H, 4.72; Cl, 41.46; O, 18.71. Found: C, 34.92; H, 4.74; Cl, 41.75; O, 18.59 (difference).

***cis*-2,3-Dichloroacrylaldehyde (7).** Spontaneous hydrolysis of the crude dimethyl acetal **4** described above gave a product (**7**) which was obtained in pure form by gas chromatographic separation. Reduction of **7** with $LiAlH_4$ in diethyl ether[2] gave the known *cis*-2,3-dichloroallyl alcohol.[21] The liquid film infrared spectrum of **7**, $n^{25.1}D$ 1.4980, in the NaCl region shows vinyl CH at 3055 (s); aldehydic CH at 2835 (m,b) and 2715 (w,b); C=O at 1705 (vs); C=C at 1583 (vs); and other bands at 1384 (m), 1287 (m,b), 1128 (vs), 870 (s), 812 (m,b) 706 (w), 674 (s), and 636 (s) cm^{-1}. The nmr spectrum of **7** in CCl_4 shows singlet resonances at τ 2.57 ($C{=}C{-}H$) and 0.61 ($-CHO$).

Anal. Calcd for $C_3H_2Cl_2O$: C, 28.84; H, 1.61; Cl, 56.75; O, 12.80. Found: C, 29.06; H, 1.78; Cl, 56.51; O, 12.65 (difference).

Thermal Isomerization of Pentachlorocyclopropane (1) to 1,1,3,3,3-Pentachloropropene (8). Pentachlorocyclopropane (41.0 g, 0.19 mole) was heated to 160° for 1 hr in a 50-ml distilling flask fit with a 10-cm glass-helix-packed Bantamware column. No darkening of the pot contents occurred. The column was wrapped with heating tape and 32.0 g (78%) of colorless **8**, $n^{22.7}D$ 1.5213 ($n^{27.7}D$ 1.5202), was distilled off at 177–179° (740 mm) over a 1-hr period; 9 g of pale yellow pot residue remained. The infrared spectrum of the distillate matched that of the pot residue, and both were identical with that of **8** obtained in pure form by gas chromatography. Although **1** and **8** were *not* resolved on the silicone column, they were readily resolved on a Ucon LB550X column; **8** was eluted first. The liquid film infrared spectrum of **8** in the NaCl region shows vinyl CH at 3060 (s); C=C at 1603 (vs); and other bands at 1280 (vw), 1082 (vs,s), 939 (vs,s), 823 (vs,s), 783 (m,s), 719 (m,s), and 643 (s,s) cm^{-1}. The nmr spectrum of **8** shows a single sharp peak at τ 3.15.

Anal. Calcd for C_3Cl_5H: C, 16.81; Cl, 82.72; H, 0.47. Found: C, 16.97; Cl, 82.75; H, 0.51.

Chemical Reactions of 1,1,3,3,3-Pentachloropropene (8). On warming in *n*-butyl alcohol in the presence of Zn or $ZnCl_2$, **8** reacted vigorously to provide an 80% yield of $CCl_2{=}CH{-}CO_2$-*n*-Bu identical with authentic material.[2] On warming to 100° over (molten) 85% KOH pellets, **8** reacted quickly to provide a 60% yield of a compound **9** (C_6Cl_8). The Nujol mull infrared spectrum of **9**, mp 90.8–91.8° (from CH_3OH) (lit.[19,20] mp 93°), shows a broad complex band in the C=C region with major peaks at 1607–1603 (m, doublet) and 1570 (s); plus other bands at 1144 (m,b) 1112 (m,s), 941 (m,b), 910 (w,s), 898 (vw,s), 779 (vs,s), and 673 (m,vs) cm^{-1}. These properties are essentially identical with those of perchloro-1,2-dimethylenecyclobutane[19] obtained in the dimerization of tetrachloroallene (**10**).[20a]

Anal. (of **9**) Calcd for C_6Cl_8: C, 20.26; Cl, 79.74. Found: C, 20.56; H, nil; Cl, 79.17.

Acknowledgments. The authors thank the National Science Foundation for a grant in partial support of this work, and the National Institutes of Health for a Predoctoral Fellowship to S. W. T. They are indebted to Dr. Paul von R. Schleyer for crucial advice early in this work, and to Miss Carol Gross and Mr. Gary Krejcarek for carrying out several large-scale syntheses of pentachlorocyclopropane.

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(21) (a) L. F. Hatch, J. J. D'Amico, and E. V. Ruhnke, *J. Am. Chem. Soc.*, 74, 123 (1952); (b) L. F. Hatch and S. S. Nesbitt, *ibid.*, 72, 727 (1950).

Tetrachlorocyclopropene, Tetrabromocyclopropene, and Some Fluorinated Cyclopropenes and Cyclopropanes[1]

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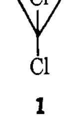
Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706. *Received December 3, 1965*

Abstract: The compound C_3Cl_4 obtained by dehydrochlorination of pentachlorocyclopropane is shown to be tetrachlorocyclopropene (**1**). **1** is converted in high yield to tetrabromocyclopropene (**2**) on treatment with BBr_3. 3-Fluoro-1,2,3-trichlorocyclopropene (**10**), 1,2-dichloro-3,3-difluorocyclopropene (**11**), and 1,2-dibromo-3,3-difluorocyclopropene (**12**) are obtained from the reaction of SbF_3 with **1** and **2**. Possible mechanisms for these halogen exchange reactions are discussed. The ultraviolet-catalyzed halogenation of the above tetrahalocyclopropenes provides perhalocyclopropanes.

The halogenated cyclopropenes represent an almost totally unexplored class of compounds.[2] As of the time of this writing the only published reference to a cyclopropene compound with covalent halogen substituents, other than preliminary reports of the work described herein,[3,4] is a note by Mahler on 1,2-bistrifluoromethyl-3,3-difluorocyclopropene (3).[5] This paper describes the proof of structure of tetrachlorocyclopropene (1), the synthesis of tetrabromocyclopropene (2) from tetrachlorocyclopropene, and the ready conversion of 1 and 2 to partially fluorinated cyclopropenes. Further chemical reactions of these compounds are outlined in separate papers.[6]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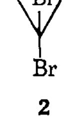
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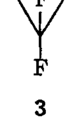
3

Tetrachlorocyclopropene (1) can be easily and efficiently obtained by the dehydrochlorination of

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[1] This paper is taken from the Ph.D. thesis of S. W. T., The University of Wisconsin, 1965.

[2] For a recent review of cyclopropene chemistry see F. L. Carter and V. L. Frampton, *Chem. Rev.*, 64, 497 (1964).

[3] S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

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

[5] W. Mahler, *ibid.*, 84, 4600 (1962).

[6] (a) S. W. Tobey and R. West, *ibid.*, 88, 2478 (1966); (b) *ibid.*, in press.

pentachlorocyclopropane (**4**).[7] **1** is a colorless, lachrymatory liquid with the odor of rotten tomatoes, bp 130–131° under N_2. The elemental analysis and molecular weight of **1** are in accord with a C_3Cl_4 formulation, but these data do not differentiate between **1** and the other two possible isomers of C_3Cl_4: tetrachloroallene ($CCl_2{=}C{=}CCl_2$, **5**), and trichloromethylchloroacetylene ($CCl_3{-}C{\equiv}CCl$). When the preparation of **1** was first carried out, neither of these compounds had been reported, and **5** in particular was considered a possible product of the dehydrochlorination of **4**.[8,9] However, the infrared and Raman spectra of **1** are in accord only with a cyclic structure for the reaction product.

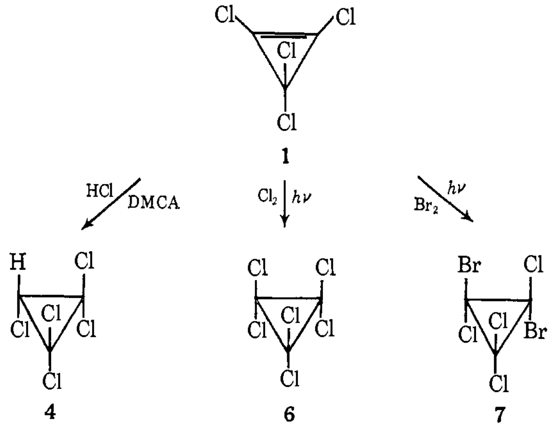
In Table I the previously published infrared spectrum of **1**[3] is compared with its observed Raman spectrum. The presence of only four strong infrared fundamentals indicates a highly symmetrical molecule. The absence of both infrared and Raman acetylenic $-C{\equiv}C-$ absorption near 2200 cm^{-1} immediately excludes the $CCl_3{-}C{\equiv}CCl$ structure.[10,11] The absence of allenic $C{=}C{=}C$ infrared absorption near 1960 cm^{-1} suggested further that **1** did not have structure **5**.[10,11] Nonetheless, since chloroallene and several symmetrically substituted allenes all show, at best, weak infrared absorption in this region,[12] **5** could not be excluded on this evidence alone. Also, **1**, like many allenes,[11] does show intense Raman emission near 1070 cm^{-1}. As Table I shows, however, **1** has a strongly polarized Raman fundamental coincident with a strong infrared fundamental at 1148 cm^{-1}. In V_d (allene) symmetry such a coincidence is forbidden.[13] In cyclopropene symmetry (C_{2v}) six coincidences of this type are predicted[14] so that compound **1** can be assigned a cyclic structure with some confidence.

Table I. The Infrared and Raman Spectra of Tetrachlorocyclopropene

Infrared spectrum,[a] frequency (cm^{-1})	Raman spectrum,[b] frequency (cm^{-})[1]
1810 (w)[c]	1811 (s) pol[d]
1300 (w)	
1190 (w)	
1148 (vs, s)	1148 (m) pol
1100 (w)	
1055 (vs, s)	1057 (w)
	939 (w)
817 (w)	
753 (vs, b)	751 (s, b)
690 (m, s)	689 (s, s)
617 (vs, s)	616 (s, b)
	554 (w, s)
	540 (m)
412 (w, b)	411 (vs, b) pol
	269 (m, s)
	142 (s, b)
	110 (s, s)

[a] Liquid film spectrum taken between NaCl and CsI plates. [b] Stokes lines of pure liquid excited by Hg 4047- and 4359-A lines. [c] The first letter in parentheses denotes the line intensity; vs = very strong, s = strong, m = medium, w = weak. The second letter in parentheses denotes the line width; s = sharp, b = broad. [d] pol = polarized Raman line.

Unequivocal chemical proof of the cyclic structure of **1** is provided by the fact that chlorination of **1** in ultraviolet light converts it rapidly and exclusively to hexachlorocyclopropane (**6**).[15] Furthermore, on hydrochlorination in dimethylacetamide **1** reverts in high yield to pentachlorocyclopropane.[3,16,17] Bromination of **1** in ultraviolet light converts it to a 1,2-dibromotetrachlorocyclopropane (**7**), probably the *trans* isomer.



The frequency of the $C{=}C$ stretching band in the vibrational spectrum of tetrachlorocyclopropene is noteworthy. As shown in Table I, tetrachlorocyclopropene shows only one infrared band anywhere near 1600 cm^{-1}, and that is a very weak absorption at 1810 cm^{-1}. The coincidence of this infrared band with a strong, polarized Raman line permits immediate assignment of the 1810-cm^{-1} band to the vibrational mode of **1** that involves symmetrical $C{=}C$ stretching,[14,19] even though the band lies nearly 200 cm^{-1} above the corresponding frequency of normal chlorinated olefins.[20] This rather large displacement results from the fact that in the case of cyclopropenes it is incorrect to consider $C{=}C$ infrared absorption as being associated with this vibration alone. As pointed out earlier by Wilcox and Craig,[21a] the absorption is due to a normal

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

[8] W. von E. Doering and A. K. Hoffman, *ibid.*, **76**, 6162 (1954).

[9] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1958, p 58.

[11] N. Sheppard and D. M. Simpson, *Quart. Rev.* (London), **6**, 1 (1952).

[12] J. H. Wotiz and D. E. Mancusco, *J. Org. Chem.*, **22**, 207 (1957).

[13] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1954, pp 253 and 339.

[14] G. Herzberg, ref 13, pp 6, 134, and 252.

[15] S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 56 (1964).

[16] Although $CCl_3C{\equiv}CCl$ remains unreported, preliminary reports on the synthesis of tetrachloroallene appeared while our characterization of tetrachlorocyclopropene was still in progress.[17,18] **5** is markedly different from **1**. It is extremely reactive, and dimerizes rapidly even at temperatures below 0°. It reacts rapidly with chlorine to give $CCl_2{=}CCl{-}CCl_3$. Tetrachloroallene does, in fact, show a very strong allenic infrared absorption at 1962 cm^{-1}.[17]

[17] K. Pilgram and F. Korte, *Tetrahedron Letters*, 883 (1962).

[18] A. Roedig, C. Märkl, and B. Heinrich, *Angew. Chem.*, **75**, 88 (1963).

[19] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

[20] L. J. Bellamy, ref 10, p 35, lists the limits for $C{=}C$ absorption at 1600–1680 cm^{-1}, but notes that fluorine substitution may raise the $C{=}C$ frequency to as high as 1800 cm^{-1}. The effect of chlorine substitution on open-chain olefins is usually to lower the position of $C{=}C$ absorption. For example, *cis*-$CHCl{=}CHCl$ absorbs at 1655, *trans*-$CHCl{=}CHCl$ at 1595, $CH_2{=}CCl_2$ at 1600, and $CCl_2{=}CHCl$ at 1595 cm^{-1}. See "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1965.

[21] (a) C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3868 (1961); (b) the $C{=}C$ infrared band for cyclopropene occurs at

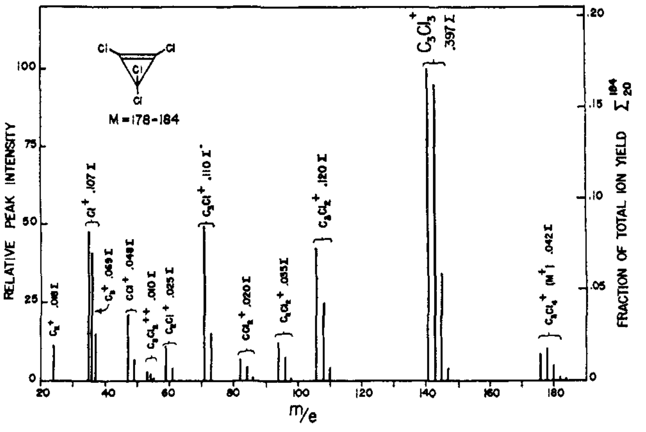


Figure 1. Mass spectrum of tetrachlorocyclopropene (**1**). The composition of each fragment is shown over the bracket which encloses all isotopic species contributing to that fragment. The integral contribution of each fragment to the total positive ion yield is also indicated. The peak height ratios under each bracket correspond to the normal Cl^{35}–Cl^{33} isotope distribution: K. Bieman, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 59-69.

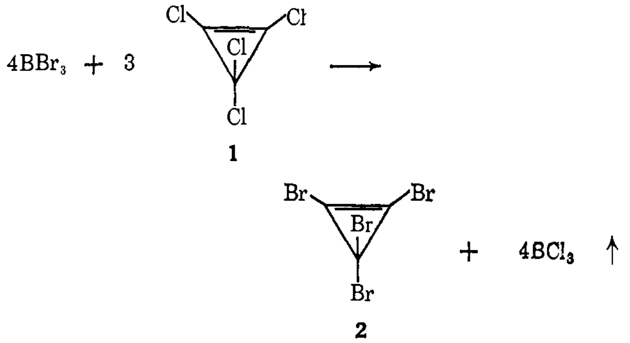
vibrational mode of the entire molecule in which the C=C vibration is strongly coupled to ring breathing and substituent vibrations. As a result the C=C absorption band in cyclopropenes wanders over an exceptionally wide range and depends heavily on the nature of the ring substituents.[21] The low intensity of the infrared C=C absorption band in **1** is in accord with the expectation that activation of this mode should cause at best only a small change in the molecular dipole moment.

The ultraviolet spectrum of **1** in isooctane shows rapidly rising absorption below 270 mμ which shifts downward toward 230 mμ as the concentration of **1** is decreased. This behavior resembles that of CCl_4 and a variety of other chlorinated olefins and paraffins in the same region[22] and is due simply to the presence of C—Cl bonds. Any electronic transitions involving the C=C in **1** probably occur below 200 mμ.[19]

The most abundant peaks in the mass spectrum of tetrachlorocyclopropene are shown in Figure 1. The prominent $C_3Cl_3^+$ ion in the mass spectrum is probably the trichlorocyclopropenium ion, since this ion can be obtained very readily from **1** by chemical means.[4,6a]

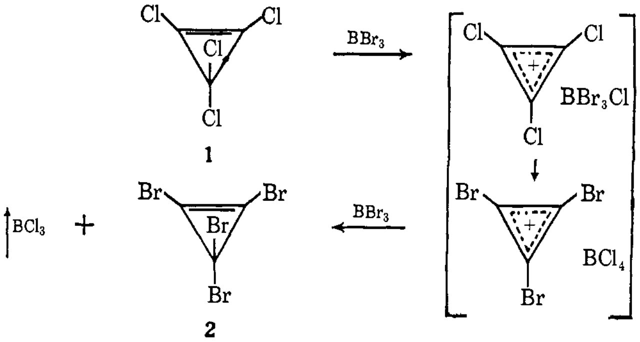
Tetrabromocyclopropene

Tetrabromocyclopropene can be obtained in almost quantitative yield from tetrachlorocyclopropene simply by treating it with BBr_3. This remarkable reaction is qualitatively different from that observed when tetrachlorocyclopropene is warmed with strong Lewis acids such as $AlCl_3$, $SbCl_5$, and $FeCl_3$, since in these reactions stable trichlorocyclopropenium ion salts are generated.[4] Although neither BCl_3 nor BF_3 have any apparent effect on **1** when they are bubbled through it at 25°, the addition of BBr_3 to **1** at 25° or above causes a vigorous exothermic reaction. No cyclopropenium ion salt precipitates, but gaseous BCl_3 is evolved instead. The reaction proceeds rapidly up to the point where almost all the tetrachlorocyclopropene is converted to tetrabromocyclopropene according to the equation



After addition of the stoichiometric amount of BBr_3 the reaction stops abruptly. Furthermore, addition of BBr_3 to purified **2** causes no apparent further reaction. In the reaction shown, gas chromatographic analysis of the product shows only peaks for **1** and **2**. Attempts to generate mixed chlorobromocyclopropenes by running the reaction at lower temperatures and with a deficiency of BBr_3 have been unsuccessful.

Three kinetic and thermodynamic arguments can be used to explain the rapid selective conversion of **1** to **2**. First, the reaction occurs in a low dielectric constant medium. This means that even though the reaction probably goes *via* an ionic mechanism involving the initial formation of $C_3Cl_3^+BBr_3Cl^-$, as shown below,[4] this intermediate most likely exists as a transient ion pair with little opportunity for cation–anion separation. If so, very rapid preferential exchange of three halogen atoms within the solvent cage could occur, making the $C_3Br_3^+BCl_4^-$ ion pair shown the first species of appreciable lifetime. Reaction of this ion pair with more BBr_3 would lead immediately to the observed products.



Second, even if intermediate chlorobromocyclopropenium ions are formed, and the over-all reaction is reversible, loss of the volatile BCl_3 (bp 12.5°) from the reaction mixture would drive the reaction to completion.

Third, as shown in Table II, for each mole of halogen exchanged in the above reaction, approximately 9 kcal of heat is evolved, so that the over-all reaction is rather strongly favored by approximately 36 kcal in the direction shown.

The inherent stability of the halogenated cyclopropenium ions must also be an important kinetic factor in the reaction. CCl_4 is quite inert toward BBr_3, and

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1641 cm^{-1};[19] (c) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 1003 (1961), and **85**, 99 (1963), list C=C infrared bands for a number of hydrocarbon cyclopropene derivatives: 3,3-dimethylcyclopropene, 1632, 1,3,3-trimethylcyclopropene, 1768, and tetramethylcyclopropene, 1865 cm^{-1}; (d) the C=C infrared band for **3** is at 1820 cm^{-1};[6] C=C absorption frequencies of additional partially fluorinated cyclopropenes are given later in this paper.

(22) J. R. Lacher, L. E. Hummel, E. F. Bohmfalk, and J. D. Park, *ibid.*, 72, 5487 (1950).

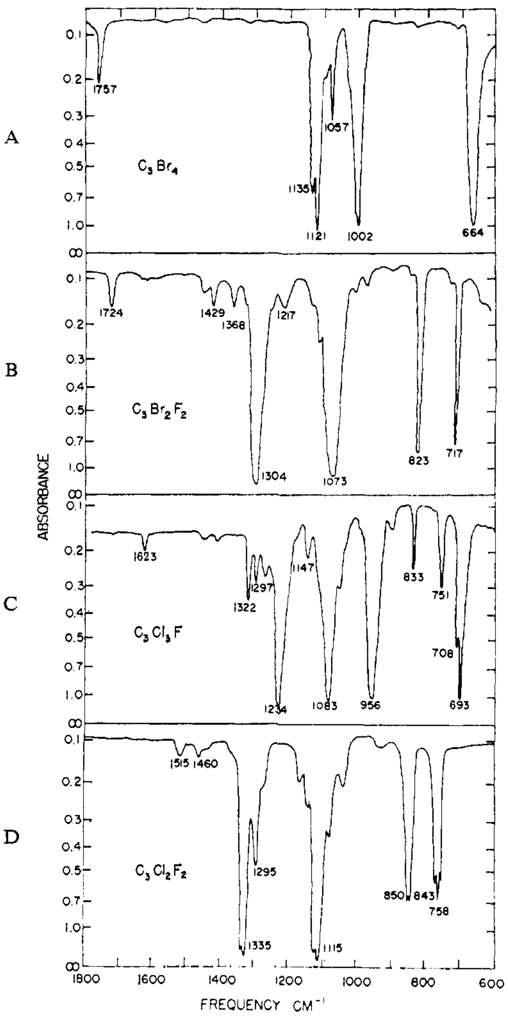


Figure 2. Infrared spectra of halogenated cyclopropenes: A, tetrabromocyclopropene (**2**), liquid film; B, 1,2-dibromo-3,3-difluorocyclopropene (**12**), liquid film; C, 3-fluoro-1,2,3-trichlorocyclopropene (**10**), liquid film; D, 1,2-dichloro-3,3-difluorocyclopropene (**11**), gas phase, P = 10 mm.

even $CCl_2{=}CCl{-}CCl_3$ which should form the perchloroallylic cation $^{\delta+}CCl_2{=}CCl{=}CCl_2^{\delta+}$ reacts only very sluggishly with BBr_3. These compounds are thermodynamically as likely as **1** to react with BBr_3, but evidently the required intermediate cations are energetically much less accessible than trihalocyclopropenium ions.

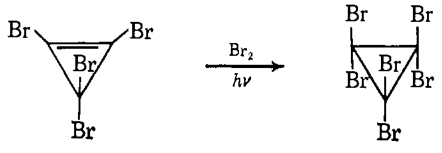
Table II. Thermodynamics of the Cyclopropene Halogen Exchange Reaction

Bond	~B—Br +	~C—Cl →	~C—Br +	~B—Cl
$\Delta H_{\text{bond}}{}^{298\,°K}$	+90	+78	−68	−109 = −9 ↑
Ref compd[a]	BBr_3	CH_3Cl	C_2H_5Br	BCl_3

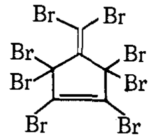
[a] Values taken from T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co. (Publishers) Ltd., London, 1954, Table 11.5.1, pp 270–289.

Tetrabromocyclopropene is a colorless, mildly lachrymatory liquid. It decomposes on attempted atmospheric pressure distillation, but it can be conveniently purified either by high-vacuum distillation (bp 95° (0.4 mm)) or by preparative gas chromatography. The infrared spectrum of **2**, as shown in Figure 2A, is very similar to that of tetrachlorocyclopropene.[3] The C=C band of **2** at 1757 cm⁻¹ is shifted 53 cm⁻¹ down from the 1810-cm⁻¹ position for **1**.

Treatment of **2** with Br_2 under ultraviolet light converts it rapidly and exclusively to hexabromocyclopropane (**8**),[4] a white, crystalline solid. The thermal stability of tetrabromocyclopropene is much lower than that of tetrachlorocyclopropene. Although vapors of **1** can be heated to 200° without decomposition, tetrabromocyclopropene decomposes vigorously if heated above 110°, even under an N_2 blanket. This exothermic reaction provides mostly tar and Br_2. However, a small quantity of a white, crystalline C_6Br_8 isomer (**9**), mp 248–251°, is formed. This material is not the C_6Br_8[23] reported to be octabromo-1,2-dimethylenecyclobutane,[24] prepared *via* the dimerization of $CBr_2{=}C{=}CBr_2$, since this latter material has a melting point of 131°. The physical and spectral properties of **9** are very similar to those of 3-chloro-heptabromo-1-methylene-3-cyclopentene,[25] and **9** has been tentatively assigned an octabromo-1-methylene-3-cyclopentene structure.



2 **8**



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Fluorocyclopropenes

The fact that allylic halogens in larger ring and open-chain alkenes are known to be rapidly exchanged for fluorine on treatment with SbF_3[26] suggested that some of the halogens in tetrachlorocyclopropene and tetrabromocyclopropene might undergo an analogous reaction and provide fluorocyclopropenes. Rapid heating of **1** with excess SbF_3 at 90–115° in Pyrex apparatus does in fact provide mixtures of 3-fluoro-1,2,3-trichlorocyclopropene (**10**) and 1,2-dichloro-3,3-difluorocyclopropene (**11**). No ring-opened volatile products are evolved. At 92° the over-all recovery of cyclopropene compounds is only 67%. Fluorinated products constitute 78% of the distillate and the ratio of **11** to **10** is 2.2 to 1. At 115° over-all recovery rises to 85%, but fluorinated products comprise only 50% of the distillate, and the ratio of **11** to **10** falls to 1.2 to 1. This suggests that the monofluorocyclopropene **10** is the initial reaction product. At 115° this product distils off before further reaction with SbF_3 can occur. At 92° an appreciable concentration of **10** builds up in the reaction mixture and further reaction with SbF_3

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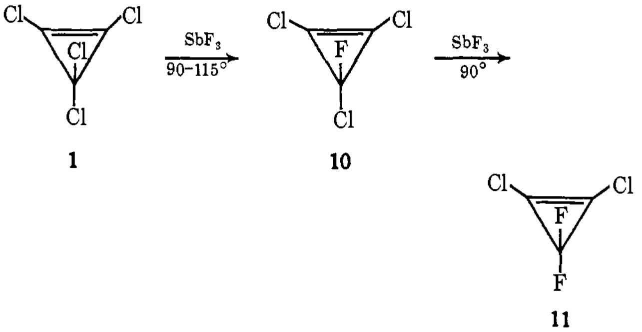
(23) See A. Roedig, J. Brandmüller, and E. Ziegler, *Naturwissenschaften*, **49**, 466 (1962), for a compendium of all possible C_6X_8 structures.

(24) A. Roedig, N. Detzer, and H. J. Friedrich, *Angew. Chem. Intern. Ed. Engl.*, **3**, 382 (1964).

(25) E. T. McBee, C. W. Roberts, and K. Dinbergs, *J. Am. Chem. Soc.*, 78, 491 (1956).

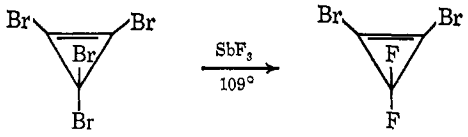
(26) (a) A. Latif, *J. Indian Chem. Soc.*, **30**, 524 (1953); (b) A. L. Henne, A. M. Whaley, and J. K. Stevenson, *J. Am. Chem. Soc.*, **63**, 3478 (1941).

to provide **11** takes place. No tri- or tetrafluorocyclopropenes have been detected in any of these reactions, nor in other experiments where SbCl$_5$ was added. That the fluorine in **10** is located on the 3 position is shown by the fact that hydrolysis of **10** in the presence of SbCl$_5$ and a trace of moisture provides CHCl=CCl—COF.[27]



1 **10** **11**

On warming **2** with excess SbF$_3$ to 109°, 1,2-dibromo-3,3-difluorocyclopropene (**12**) distils off in 51% yield. No monofluoride is observed, most probably because the reaction was carried out at a low temperature relative to its boiling point. No tri- or tetrafluoride was evolved, nor any ring-opened products.



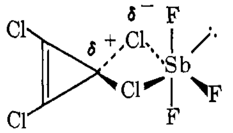
2 **12**

The geminal (3,3) location of the fluorines in **11** and **12** is unambiguously demonstrated by the structure of the F^{19} nmr patterns. The spectrum of **11** shows a sharp singlet peak 11.7 ppm downfield from internal TCTFCB,[28] showing that the fluorines are symmetry equivalent (either 1,2 or 3,3). The F^{19} spectrum of pure **11** shows *singlet* C^{13} satellites flanking the main resonance and separated by 292 ± 3 cps.[29] This pattern is consistent only with geminal location of the fluorines. In the alternate 1,2-difluoro structure for **11** the C^{13} side bands would be *doublets*, characteristic of an AMX system.[30] The F^{19} nmr spectrum of **12** shows a singlet peak 13.39 ppm below TCTFCB, again with singlet C^{13} side bands, spaced at 320 cps. The observed C^{13}–F coupling constants in the CF$_2$ groups of **11** and **12** are similar to the 329-cps coupling constant in hexafluorocyclopropane.[31]

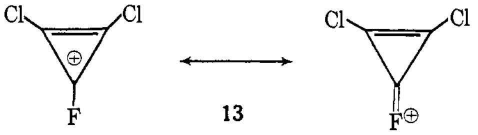
To the extent that cyclopropenes resemble other alkenes, the >CX$_2$ halogens in **1** and **2** may be considered to be allylic and the $=\overset{|}{\mathrm{C}}\mathrm{-X}$ halogens vinylic. If this similarity is accepted, the observed conversions of **1** and **2** to **11** and **12** are just what would be anticipated. In larger ring and open-chain, highly chlorinated alkenes, allylic chlorines are strongly activated and undergo facile replacement by fluorine using SbF$_3$, whereas vinylic halogens are uniformly inert.[32] That activation of the geminal halogens in **1** and **2** by the cyclopropene double bond is important is shown by the fact that the >CCl$_2$ group of **1** is considerably more reactive than the >CCl$_2$ groups on hexachlorocyclopropane.[15] Treatment of **6** with SbF$_3$ for several minutes at 110° causes no discernible reaction.[33]

The activation of halogens in allylic positions is thought to be caused by the inherent stability of the allylic cation which develops while the halide ions are undergoing exchange. Halogen exchange in cyclopropanes is undoubtedly strongly assisted by the ease of formation of the trihalocyclopropenium ion. However this explanation fails to explain why cyclopropenes substituted with fluorine at the 1 and 2 (vinylic) positions are not obtained. Either of the following two extensions of the above explanation rationalize the observed specificity of the reactions of SbF$_3$ with **1** and **2**.[34]

If the reaction involves halogen exchange only within the coordination sphere around a pentacoordinated antimony[35] in which *two* halogen ligands from the substrate are required the halogen exchange would be assisted by the inherent stability of the developing cyclopropenium ion, as shown below. However the uncomplexed ion would *not* exist and selective replacement of *geminal* halogens *only* would be predicted.[36]



Alternatively, if the reaction involves *free* cyclopropenium cations then the fluorodichlorocyclopropenium ion formed from **10** must simply react further only at the carbon bearing the fluorine. Further reaction at this site should be favored by the small size of the fluorine, and its greater ability than chlorine to stabilize an electron-deficient carbon center by p$_\pi$–p$_\pi$ back bonding.[37] Localization of charge at the C–F center as shown in **13** would promote subsequent nucleophilic attack there.



13

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[27] For details on this compound and the implications of its structure on that of **10** see ref 6b.

[28] 1,1,2,2-Tetrafluoro-3,3,4,4-tetrachlorocyclobutane; see G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[29] N. Muller and D. T. Carr, *ibid.*, **67**, 112 (1963), discuss the factors involved in C^{13}–F coupling. The expected 5–6-cps shift in the center of gravity of the C^{13} side-band spectrum away from the main resonance was just barely detectable.

[30] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, pp 61–88.

[31] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

[32] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, pp 8, 9.

[33] Chlorines on unconjugated carbon atoms are generally of low reactivity; see R. Stevens and J. C. Tatlow, *Quart. Rev.* (London), **16**, 44 (1962), and M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Pergamon Press, Ltd., London, 1961, p 93.

[34] Arguments entirely analogous to those presented here can be used to rationalize the fact that on treatment with SbF$_3$ at 150° CCl$_2$=CCl—CCl$_3$ gives *only* CCl$_2$=CCl—CFCl$_2$, CCl$_2$=CCl—CClF$_2$, and CCl$_2$=CCl—CF$_3$ with no trace of compounds containing vinyl fluorine. See ref 26b for details of this experiment.

[35] G. E. Coates, "Organometallic Compounds," 2nd ed, Methuen and Co., Ltd., London, 1960, pp 214–221.

[36] Some support for this postulate is provided by the fact that while (in general) both CCl$_3$ and CHCl$_2$ groups can be converted to their fluoro analogs using SbF$_3$, the CH$_2$Cl group cannot; see A. L. Henne, *Org. Reactions*, **2**, 54 (1944), and also H. S. Booth and C. F. Swinehart, *J. Am. Chem. Soc.*, **57**, 1333 (1935).

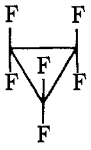
[37] J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 36–46.

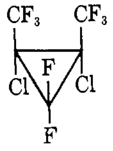
The infrared spectra of **10**, **11** and **12** are shown in Figures 2B, 2C, and 2D. Note that **10**, which differs from **1** only in having a fluorine rather than chlorine at a location remote from the double bond, shows a "C=C" frequency *lower* by 185 cm^{-1}.

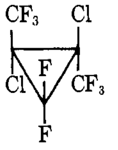
The gas-phase infrared spectrum of **11** shows *no* "C=C" band at all. In this compound activation of the mode containing symmetrical C=C vibration causes such a small change in the dipole moment that the infrared absorption, though allowed by C_{2v} symmetry, is not observed. In C_{2v} symmetry this same vibrational mode should result in a very strong, highly polarized Raman band at the same frequency, and a band of this type *is* observed in the Raman spectrum of **11** at 1760 cm^{-1} below the exciting line. Comparing this frequency with the 1625 cm^{-1} absorption characteristic of **10** shows that replacement of the *second* methylene chlorine with fluorine results in a 135 cm^{-1} *increase* in frequency. These data illustrate further the fact that C=C stretching in cyclopropenes is very strongly coupled to other vibrations.[21] The infrared spectrum of **12** is very similar to that of **11** except that a C=C band *is* now observed, located at 1724 cm^{-1}. **10**, **11**, and **12** all show strong C–F vibrations between 1250 and 1350 cm^{-1}.[38]

Fluorocyclopropanes

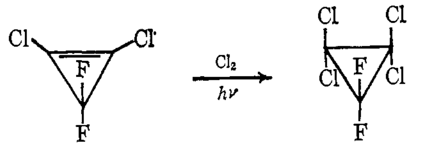
Hexafluorocyclopropane (**14**),[39] and *cis*- and *trans*-1,2-bistrifluoromethyl-1,2-dichloro-3,3-difluorocyclopropane (**15** and **16**) obtained by Mahler[5] in the chlorination of **3**, are the only reported fluoro-substituted cyclopropanes. A large number of mixed fluorobromochlorocyclopropanes can be generated from **11** and **12** by simple halogenation of the double bond.


14


15


16

One compound of this type is described here. Chlorination of **11** under ultraviolet light converts it to 1,1-difluorotetrachlorocyclopropane (**17**). Unlike other polyhalocyclopropanes[15] **17** is a liquid, boiling at 121° (740 mm). The infrared spectrum of **17** shows a singlet resonance for the $>\text{CF}_2$ group at 19.5 ppm *upfield* from TCTFCB, corresponding to a 31.2-ppm upfield shift from the resonance position of the fluorines in the unsaturated starting material **11**.[40] The singlet C^{13} side bands on the main resonance peak for **17** show $J_{C_{13}\text{-F}}$ = 313 cps which resembles closely the 329-cps coupling constant in **14**.[31]



11 **17**

Experimental Section

All syntheses were carried out using purified grades of commercially available starting materials. Gas chromatographic separations were carried out on a Wilkins Instrument and Research, Inc., Aerograph A-90 thermoconductivity detector intrument at 155–165° using helium carrier gas at a flow rate of 80 ml/min through 5 ft × 0.5 in. columns packed with silicone Dow 11 or G.E.S.F.-96 (20%) on 30–60 mesh firebrick. Melting points are sealed capillary values and are corrected to within ±1°. Boiling points were determined by a capillary tube method,[41] and are corrected to within ±1°. Infrared spectra in the region 4000–625 cm^{-1} were taken between NaCl plates on a Perkin-Elmer Model 237 recording spectrophotometer calibrated in cm^{-1}. Infrared spectra in the region 650–300 cm^{-1} were taken between CsI plates on a Perkin-Elmer Model 112 single-beam spectrometer equipped with CsBr prism. Band positions were assigned from a predetermined calibration curve. Listed infrared frequencies are correct within ±3 cm^{-1}. Raman spectra were recorded on a Cary Model 81 recording spectrometer in 7 mm o.d. × 24 cm Pyrex cells with 12 mm o.d. bulbous front windows. Mass spectra were determined on a CEC 21-110 spectrometer using 70-ev ionizing electrons with the inlet temperature at 175° and the source at 50°. F^{19} nmr spectra were recorded on a Varian Associates HR-60 spectrometer operating at 56.4 Mc. Fluorine chemical shift values were determined on 10% (v/v) solutions of organic liquid in CCl_4 which contained 2% (w/v) dissolved TCTFCB.[28] A sealed capillary of pure liquid $\text{CF}_3\text{CO}_2\text{H}$ was inserted for use in adjusting the magnetic field. The TCTFCB uniformly resonated at 1950 ± 5 cps *above* the external $\text{CF}_3\text{CO}_2\text{H}$. Reported chemical shifts are relative to internal TCTFCB and were obtained by interpolation between side bands generated on TCTFCB or $\text{CF}_3\text{CO}_2\text{H}$ using an external variable frequency oscillator with digital readout. Shift values reported are the average of values obtained with increasing and decreasing field, and were reproduced to ±3 cps. C^{13}–F satellites were observed using pure liquid samples with external $\text{CF}_3\text{CO}_2\text{F}$ using the techniques outlined above. For maximum accuracy in locating the C^{13} side-band positions, the instrument gain was not adjusted during sweeps. This caused the central resonance to be quite wide and off recorder scale at the peak, thus obscuring its exact location.[29] Elemental analyses were performed in the Microanalytical Laboratory of Dr. Alfred Bernhardt at the Max Planck Institut für Kohlenforschung.

Tetrachlorocyclopropene (1). Pentachlorocyclopropane[7] (50 g, 95 mole %, 5% 1,2-dimethoxyethane, 0.22 mole) was added to 0.6 mole of KOH dissolved in 40 ml of water. After swirling for 30 min, during which time the reaction temperature was kept between 85–95° by occasional cooling, the loose emulsion reaction mixture was cooled to 50° and 50 ml of cool water was added. On adding 25 ml of cold concentrated HCl the pH of the solution fell below 2 and the emulsion broke. The lower oily layer (25 ml) was separated off and dried briefly over CaCl_2. Simple distillation of the oil into receivers at 0° under N_2 provided 33.0 g (0.185 mole, 85%) of clear, colorless **1** boiling between 129 and 133° (nearly all 130–131°) at 745 mm. A 1-ml forerun was arbitrarily rejected and less than 3 ml of light yellow higher boiling residue remained in the still pot. Gas chromatographic analysis of the distillate showed less than 1% of a single, lower boiling impurity. The infrared spectrum of **1**, $n^{25.0}\text{D}$ 1.5065, is shown in ref 3. The Raman spectrum of **1** is tabulated in Table I. The molecular weight of **1** at 200°[42] was 179 ± 3 (calcd for C_3Cl_4, 177.8).

Anal. Calcd for C_3Cl_4: C, 20.26; H, 0.00; Cl, 79.74. Found: C, 20.23, 20.28; H, nil; Cl, 79.69, 79.72 (duplicate analyses).

Chlorination of 1 to Hexachlorocyclopropane (6).[15] Tetrachlorocyclopropene (0.5 g) was irradiated with a G.E. H4 Hg arc from a distance of 7 cm in a small quartz flask fitted with a reflux condenser through which a slow flow of Cl_2 was admitted *via* a capillary. Clear crystals began forming on the flask wall nearest the lamp immediately, and after 15 min essentially no liquid remained in the flask. Gas chromatographic analysis of the reaction products dissolved in 0.2 ml of CCl_4 showed just three well-separated peaks of which the first and largest was CCl_4, the second small peak being unreacted **1**, and the third large peak being pure hexachlorocyclopropane (infrared analysis).

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[38] L. J. Bellamy, ref 10, pp 328–330.

[39] J. Harmon, U. S. Patent 2,404, 374 (1946); *cf. Chem. Abstr.*, 40, 7234 (1946).

[40] Mahler[5] does not list the F^{19} resonance positions of the analogous pairs 3:15 and 3:16.

[41] N. D. Cheronis, "Technique of Organic Chemistry," Vol. VI, Interscience Publishers, Inc., New York, N. Y., 1954, p 190.

[42] R. Livingston, "Physico Chemical Experiments," 3rd ed, The Macmillan Co., New York, N. Y., 1957, pp 53–55.

Hydrochlorination of 1 to Pentachlorocyclopropane (4).[3,7] Tetrachlorocyclopropane (1.55 g, 0.0087 mole) was dissolved in 2.62 g of dimethylacetamide and warmed to 70°. Introduction of gaseous HCl *via* a capillary bubbler brought the reaction mixture rapidly to 120° with very little HCl being evolved from solution. After 10 min HCl evolution from solution began abruptly, the reaction temperature fell quickly to 90°, and HCl introduction was stopped. The reaction mixture had increased in weight 1.62 g due to absorption of 0.0445 mole of HCl. The pale yellow, viscous mixture was diluted with 15 ml of water, throwing down a colorless oil which when drawn off and dried over $CaCl_2$ weighed 1.40 g. Gas chromatographic analysis of this oil showed just one sharp peak for **4** (infrared analysis). The yield of **4** was 76%.

Bromination of 1 to *trans*-1,2-Dibromotetrachlorocyclopropane (7). Tetrachlorocyclopropene (7.2 g, 0.040 mole) in a quartz flask was irradiated with a Hanovia Hg arc from a distance of 4 cm for 1 hr. Bromine was added as fast as it was consumed. The resulting pink, crystalline product mass when recrystallized from CH_3OH provided 8.5 g (0.025 mole, 63%) of **7**, mp 118.5–120.0°. The Nujol mull infrared spectrum of **7** in the NaCl region shows bands at 936 (w), 894 (s), 873 (w), 810 (vs, s), and 780 (m) cm^{-1}. Compound **7** reacted vigorously with Zn in EtOH to produce *cis*-CHCl=CCl-CO_2Et[15] as the only isolable product. **7** has tentatively been assigned the *trans*-dibromo structure shown, since the *cis* isomer of **7** would be expected to provide either ester products containing bromine, or the same spectrum of products that hexachlorocyclopropane produces under these conditions.[15]

Anal. Calcd for $C_3Cl_4Br_2$: C, 10.67; Cl, 42.00; Br, 47.33. Found: C, 10.72; Cl, 41.85; Br, 47.44.

Tetrabromocyclopropene (2). Tetrachlorocyclopropene at 25° (19.43 g, 0.109 mole) was placed in a 50-ml flask fit with a reflux condenser loosely plugged with cotton and a rubber septum side-arm injection port. BBr_3 was injected in 2-ml portions from a syringe lubricated with Kel-F grease. Addition of each portion of BBr_3 caused vigorous reaction and evolution of much BCl_3 from the condenser mouth. The reaction temperature rose quickly to 40° and remained at 40–60° during the remainder of the reaction. The pot contents gradually turned pale yellow. Reaction ceased abruptly after 12.8 ml (33.9 g, 0.135 mole) of BBr_3 had been injected. After volatile material was flashed off the reaction product at 5 mm, the residual tetrabromocyclopropene distilled between 70 and 95° (0.1–0.4 mm) to give 34.25 g of colorless product (88% of theoretical based on C_3Cl_4). Gas chromatographic analysis of this distillate showed only one sharp peak for **2**. The infrared spectrum of **2** in the NaCl region, $n^{25.1}$D 1.6344, is shown in Figure 2A. The low-frequency infrared spectrum of **2** shows additional bands at 488 (m) and 464 (s, b) cm^{-1}.

Anal. Calcd for C_3Br_4: C, 10.12; Br, 89.88. Found: C, 10.53; H, nil; Br, 89.01.

Hexabromocyclopropane (8).[4] Tetrabromocyclopropene (8.75 g, 0.0246 mole) and Br_2 (4.0 g, 0.025 mole) were irradiated in a quartz flask for 50 min with a Hanovia Hg arc from a distance of 7 cm. The crystalline reaction product, colored by excess Br_2, ultimately provided 7.60 g (0.0148 mole, 60% yield) of hexabromocyclopropane, mp 194–196°, on recrystallization from acetone. The infrared spectrum of **8** in the 2000–300-cm^{-1} region shows bands at 892 (vw), 862 (s), 767 (vw), 719 (vs), 677 (s), 651 (m,b), 527 (vw), and 492 (vs, b) cm^{-1}.

Anal. Calcd for C_3Br_6: C, 6.80; Br, 93.20. Found: C, 7.08; H, nil; Br, 93.05.

Pyrolysis of Tetrabromocyclopropene. Tetrabromocyclopropene (33 g) which had been shaken with water and dried carefully over $CaCl_2$ during work-up was heated under N_2 in a simple distilling apparatus to a temperature of about 125°. A violently exothermic reaction started which caused much of the C_3Br_4 to froth over into the receiver along with a considerable amount of Br_2. The pot contents became increasingly hot and finally set to a tarry coke. On cooling, the "distillate" deposited a few pink crystals which were filtered off and crystallized from CCl_4 providing, at last, 50 mg of white, crystalline **9**. This material showed sharp, infrared bands (Nujol mull) in the NaCl region at 1603 (vs), 1569 (m), 1170 (m), 1136 (m), 1123 (s), 855 (m), 767 (m), 756 (s), and 743 (s) cm^{-1}. Compound **9** melts at 248–251° with decomposition starting at 235°. These properties are quite like those of 3-chloroheptabromo-1-methylene-3-cyclopentene[25] which shows two C=C bands at 1609 and 1565 cm^{-1}, and melts at 240–248° with sintering above 225°. Gas chromatographic analysis of the "distillate" obtained above showed several small peaks with short retention times, a major peak for tetrabromocyclopropene, and a very small peak with a very long retention time which proved to be **9**. Leaching the pot residue with hot CCl_4 gave no additional organic material. Analysis of **9** shows it is a C_6Br_8 isomer.

Anal. Calcd for C_6Br_8: C, 10.11; Br, 89.11. Found: C, 10.24; H, nil; Br, 89.91.

Reaction of SbF_3 and Tetrachlorocyclopropene at 92°. Tetrachlorocyclopropene (31.8 g, 0.179 mole) and SbF_3 (22.1 g, 0.124 mole) were heated rapidly in a Pyrex Claisen distilling apparatus. After generation of a small amount of HCl and HF at a head temperature of 95° steady, dropwise distillation of product began and continued at 92 ± 2° for 25 min, leaving a brown semisolid in the still pot and providing 13.0 g of distillate. Gas chromatographic analysis of this distillate showed three well-spaced peaks. The first off contained **11**, the second **10**, and the third unreacted **1**. By peak area analysis the yield of **11** was estimated to be 6.5 g (0.045 mole); **10**, 2.9 g (0.018 mole); and **1**, 3.6 g (0.020 mole). This amounted to 67% recovery of cyclopropene compounds.

Reaction of SbF_3 and Tetrachlorocyclopropene at 115°. SbF_3 (25.2 g, 0.141 mole) and tetrachlorocyclopropene (20.5 g, 0.115 mole) were heated rapidly as described above until the head temperature reached 115°. Rapid distillation of product began and continued for 15 min. The distillate weighed 16.3 g and was estimated as described above to contain 3.7 g (0.026 mole) of **11**, 3.6 g (0.022 mole) of **10**, and 9.0 g (0.050 mole) of **1**. This amounted to 85% recovery of cyclopropene material.

Reaction of SbF_3 and Tetrachlorocyclopropene with Added $SbCl_5$. Tetrachlorocyclopropene (25.7 g, 0.145 mole) and SbF_3 (33.7 g, 0.188 mole) were placed in a Pyrex flask fit with a water-cooled reflux condenser vented through a U tube immersed in liquid N_2. The U tube exit was capped with a $CaCl_2$ drying tube. $SbCl_5$ (2.2 ml., 0.017 mole) was added to the pot. A self-heating reaction started immediately which was assisted by gentle warming. As reflux began in the condenser about 0.5 ml of a colorless liquid with a boiling point well below 0° collected in the U tube. This material was quantitatively transferred to a 10-cm path length gas cell and the NaCl region infrared spectrum scanned. Aside from some very minor low-intensity peaks only one strong absorption at 1030 cm^{-1} was noted. This band is characteristic of SiF_4.[43] Continued reflux of the pot at a temperature of about 60° produced no additional low-boiling distillate. Subsequent distillation of the pot contents at 75–95° as described above provided 15.0 g of product. Gas chromatographic analysis of this material showed peaks of the expected size for **11** and **1**, but only a very minor peak for **10**. However, a new major peak between **10** and **1** was observed, and material taken from this peak proved on infrared and nmr analysis to be 1,2-dichloroacrylyl fluoride[27]

3-Fluoro-1,2,3-trichlorocyclopropene (10). This material was obtained by preparative gas chromatography from mixtures of **10**, **11**, and **1** prepared as described above. **10** is a colorless liquid, $n^{25.0}$D 1.4540, capillary bp 96° (743 mm). The portion of the infrared spectrum between 4000 and 625 cm^{-1} in which **10** shows absorption is shown in Figure 2B. The F^{19} nmr spectrum of **10** shows a singlet resonance 660 cps downfield from internal TCTFCB.

Anal. Calcd for C_3Cl_3F: C, 22.33; Cl, 65.91; F, 11.77. Found: C, 22.27; H, nil; Cl, 65.94; F, 11.54.

1,2-Dichloro-3,3-difluorocyclopropene (11). This material was obtained by preparative gas chromatography from mixtures of **10**, **11**, and **1** as described above. Compound **11** is a colorless, odorless volatile liquid, $n^{25.0}$D 1.4032, capillary bp 60° (733 mm). The gas-phase infrared spectrum of **11** at approximately 10 mm in a 10-cm path length cell is shown in Figure 2C. The Raman spectrum of 2.57 g of **11**, dissolved in 4.72 g of CCl_4, shows bands at 199 (m, dep), 414 (vs, pol), 524 (vw, dep), 563 (m, dep), 585 (s, pol), 671 (w, dep), 840 (w, pol), 1087 (vw, dep), 1122 (vw, pol), and 1760 (s, pol) cm^{-1} below the 4358-A Hg exciting line. In addition, the expected bands at 218 (vs, dep), 315 (vs, dep), 459 (vs, pol), 761–792 (doublet, s, dep), and 1540 (vw, pol) cm^{-1}, characteristic of CCl_4, were observed.[44] The F^{19} resonance spectrum of **11** in CCl_4 shows a singlet peak 661 cps below TCTFCB. The spectrum of pure liquid **11** shows singlet C^{13} satellites flanking the main resonance and separated by 292 cps.

Anal. Calcd for $C_3Cl_2F_2$: C, 24.86; Cl, 48.92; F, 26.22. Found: C, 24.95; H, nil; Cl, 48.85; F, 26.08.

1,2-Dibromo-3,3-difluorocyclopropene (12). Tetrabromocyclopropene (11.84 g, 0.0333 mole) and SbF_3 (9.46 g, 0.0528 mole) were heated together in a Pyrex Claisen distilling apparatus to 60°

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[43] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).

[44] G. Herzberg, ref 13, pp 250, 310–312.

for 5 min, and then brought slowly to 120°. At this point a small amount of HBr was evolved, product distillation began, and the head temperature fell to 108–109°. Distillation continued at this temperature for 5 min, then stopped abruptly, providing 4.02 g of distillate. Gas chromatographic analysis of this product showed only one peak, which proved to be **12**. The yield was 0.0169 mole or 51% of theoretical. The infrared spectrum of **12** is shown in Figure 2D. Gas chromatographically purified **12** was a colorless liquid with a pleasant minty odor with $n^{25.0}\text{D}$ 1.4757 and capillary bp 105° (742 mm). The F^{19} nmr spectrum of **12** shows a singlet resonance 761 cps below internal TCTFCB flanked by singlet C^{13} satellites spaced 320 ± 5 cps.

Anal. Calcd for $C_3Br_2F_2$: C, 15.41; Br, 68.34; F, 16.25. Found: C, 15.62; H, 0.09; Br, 68.19; F, 16.53.

1,1-Difluorotetrachlorocyclopropane (17). 1,2-Dichloro-3,3-difluorocyclopropene (**11**, 1.70 g) was irradiated with a Hanovia Hg arc at a distance of 8 cm in a quartz flask fit with a water-cooled reflux condenser through which a slow stream of Cl_2 was delivered into the liquid *via* a microcapillary. Beading of volatile liquid on the flask walls stopped after 20 min and the reaction was shut down. Loss of material by volatilization had occurred since the final flask contents weighed only 1.2 g. Gas chromatographic analysis of the residual product material revealed no peak for unreacted **11**, a large sharp peak for **17**, and a peak about one twentieth as large at a much longer retention time. This latter material (**18**) was a soft, waxy solid, Compound **17** is a colorless liquid with a pleasant, fruity odor. When purified by gas chromatography **17** had $n^{25.0}\text{D}$ 1.4447 and capillary bp 121° (740 mm). The liquid film infrared spectrum of **17** in the NaCl region shows bands at 1448 (w), 1422 (m), 1402 (vs, s), 1352 (w), 1259–1262 (doublet, vs, s), 1179 (vw), 1132 (vw), 1029 (vw), 1009 (vs, s), 941 (s, vs), 906 (vs, s), and 745 (vs, s) cm^{-1}. The F^{19} nmr spectrum of **17** shows a singlet resonance at 1101 cps above TCTFCB with singlet C^{13} side bands spaced 313 cps.

Anal. Calcd for $C_3Cl_4F_2$: C, 16.69; Cl, 65.70; F, 17.61. Found: C, 16.66, 16.56; H, 0.11, 0.17; Cl, 65.78, 65.59; F, 17.43, 17.48 (duplicate analysis).

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Synthesis of Trihalocyclopropenium Salts and Normal Coordinate Analysis of $C_3Cl_3^+$

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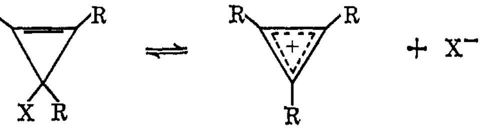
Abstract: The stable 1:1 adducts formed between tetrachlorocyclopropene and the strong Lewis acids $AlCl_3$, $SbCl_5$, $FeCl_3$, and $GaCl_3$ are shown to be salts of the trigonal planar trichlorocyclopropenium ion, $C_3Cl_3^+$, and the respective chloro anions. Tetrabromocyclopropene reacts with $AlBr_3$ to form $C_3Br_3^+AlBr_4^-$. Normal coordinate analysis of the vibrational spectrum of $C_3Cl_3^+$ using a Urey–Bradley force field gives a value for the C–C stretching force constant of 6.3 mdynes/A, substantially larger than for benzene and other six-electron aromatic species. The implications of this finding are discussed.

In pioneering experiments by Breslow and co-workers it was shown that the triphenylcyclopropenium ion (**1**) could be isolated as a stable fluoroborate salt.[1] This finding was in accord with and lent credence to the validity of molecular orbital calculations which indicated[2] that the cyclopropenium nucleus should be a stable delocalized system.[3] In this early work electron stabilization of the cyclopropenium ion by π-electron delocalization involving the phenyl substituents was considered to be an important factor in permitting isolation of the ion. In more recent work, Breslow, Farnum, and their co-workers have isolated diaryl-, dialkyl-, and trialkyl-substituted cyclopropenium ions as the perchlorate and fluoroborate salts.[4] The alkyl-substituted cyclopropenium ions, which are more stable than triphenylcyclopropenium ion, are thought to be stabilized by σ inductive donation of charge into the cyclopropenium nucleus by the alkyl substituents.[4]

In all the above work primary attention has been focused on the role of the organic groups attached to the cyclopropenium nucleus in permitting the isolation of ionic salts. However, successful isolation of cyclopropenium ion salts depends just as heavily on the nature of the counterion present in the system as it does on the nature of the organic substituents on the cyclopropene nucleus. The position of the ionization equilibrium shown in eq 1 will depend not only on the



(1)

2 **3**

relative "stabilities" of **2** and **3** (as determined by the nature of the R groups) but on the nature of X as well.

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