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) $\text{cm}^{-1}$. 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).

**Acknowledgments.** S. W. T. wishes to thank the National Institutes of Health for a Predoctoral Fellowship. This work was also supported by a grant from the National Science Foundation. We are indebted to Dr. Mitsuo Ito of Kyūshū University, Fukuoka, Japan, for obtaining the first Raman spectrum of tetrachlorocyclopropene, to Dr. Akira Sadô for assistance in obtaining the other Raman spectra, to Argonne National Laboratory for making their Raman equipment and technical assistance available to us, and to Mr. Joseph Wheeler for constructing the special Raman tubes used. Mr. Edward Chait of the Chemistry Department of Purdue University obtained the mass spectral data reported herein.

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

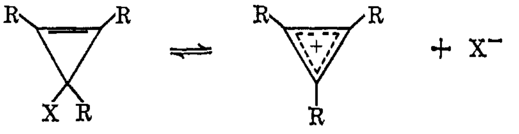
**Robert West, Akira Sadô, and Stephen W. Tobey**

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

**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 $\pi$-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 $\sigma$ 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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[1] (a) R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, 80, 5991 (1958); (b) R. Breslow, *ibid.*, 79, 5318 (1957).

[2] (a) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *ibid.*, 74, 4579 (1952); (b) J. D. Roberts, *Record Chem. Progr.*, 17, 106 (1956).

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

[4] (a) D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, 82, 2651 (1960); (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, 83, 2375 (1961); (c) R. Breslow, H. Höver, and H. W. Chang, *ibid.*, 84, 3168 (1962).

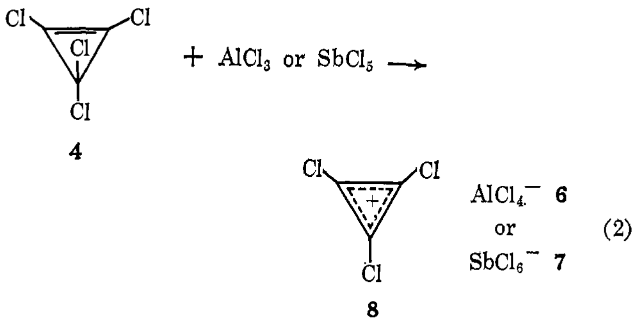
Existing data illustrate the validity of this point nicely; while the bromide, perchlorate, and tetrafluoroborate of **1** are ionic, the cyanide and methoxide of **1** behave as un-ionized, "covalent" compounds.[4]

Having synthesized tetrachlorocyclopropene (**4**) and tetrabromocyclopropene (**5**), both mobile organic liquids,[5] we were interested in determining whether or not these materials could be converted to stable salts of trihalocyclopropenium ions.[6] The simple fact that **5** is a volatile liquid while the bromide of **1** is an ionic solid clearly implies that the tribromocyclopropenium ion is a considerably stronger Lewis acid (better bromide ion acceptor) than **1**.[7] It has proved possible to generate stable salts of the trihalocyclopropenium ions, but only by the reaction of the tetrahalocyclopropenes **4** and **5** with very strong Lewis acids (halide ion acceptors). This paper describes the preparation of these salts and the normal coordinate analysis of the vibrational spectra of the $C_3X_3^+$ ions.

## Syntheses

When $AlCl_3$ is warmed in excess tetrachlorocyclopropene (**4**), an exothermic reaction starts which results in the formation of a white powder. This material on work-up shows an analysis corresponding to a 1:1 adduct $C_4Cl_3 \cdot AlCl_3$. Similarly, treatment of liquid $SbCl_5$ with excess **4** gives a white powder which proved to be another 1:1 adduct $C_3Cl_4 \cdot SbCl_5$. That the integrity of the three-membered ring is preserved in these reactions is shown by the fact that quenching either material in water regenerates **4** in 60% yield,[8] while heating dry samples of either causes **4** to distil off again in moderate yield. The vibrational spectra of these compounds, discussed in detail below, indicates that they should be formulated as the $AlCl_4^-$ (**6**) and $SbCl_6^-$ (**7**) salts of the trichlorocyclopropenium ion **8**.

The role of the Lewis acids in these reactions is simply to alter the unfavorable equilibrium dissociation of tetrachlorocyclopropene according to eq 1 to the favorable reaction shown in eq 2 *via* formation of the very stable $AlCl_4^-$ and $SbCl_6^-$ anions. The reaction of **4** with other strong Lewis acids also leads to trichlorocyclopropenium ion formation. Warming **4** with anhydrous $FeCl_3$ or $GaCl_3$ caused immediate reaction and formation of solids which on work-up proved to be the 1:1 adducts $C_3Cl_4 \cdot FeCl_3$ and $C_3Cl_3 \cdot GaCl_3$. Elemental analyses of these highly reactive compounds are unfortunately not perfect, but the results leave no real doubt as to the composition of the adducts. The NaCl infrared spectra of these adducts are essentially identical with those of **6** and **7**, showing the presence of free $C_3Cl_3^+$ ion. **4** also reacted vigorously with $AlBr_3$ on warming to generate $C_3Cl_3^+$, but this reaction was not investigated further. In the presence of weaker Lewis acids (chloride ion acceptors) ion formation does not occur. Tetrachlorocyclopropene shows no sign of reaction either on warming or long standing with $Cu_2Cl_2$, $Cu_2I_2$, $Hg_2Cl_2$, $HgI_2$, $SnCl_2$, $ZnCl_2$, $PtCl_2$, $PbCl_2$, $PBr_3$, $SbCl_3$, $BF_3$, $BCl_3$, $SnI_4$, $SnCl_4$, $PtCl_4$, or $PCl_5$. Since $AlCl_3$, $FeCl_3$, $SbCl_5$, and $GaCl_3$ abstract $Cl^-$ from **4**, but $BCl_3$ does not, the trichlorocyclopropenium ion must lie below the former but above the latter on an approximate Lewis acidity scale.



(2)

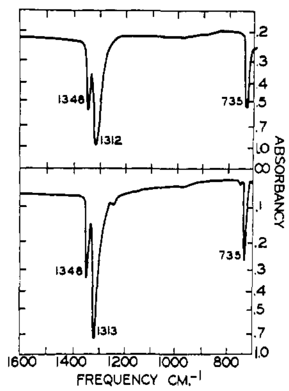


Figure 1. Infrared spectra in the sodium chloride region for $C_3Cl^+AlCl_4^-$ (A) and $C_3Cl_3^+SbCl_6^-$ (B). Mulls in Nujol, with Nujol bands deleted.

Tetrabromocyclopropene (**5**) reacts in a similar way with $AlBr_3$ in $CS_2$ to form a 1:1 adduct $C_3Br_4 \cdot AlBr_3$ (**8**), which is the tetrabromoaluminate salt of the tribromocyclopropenium ion. When this material is quenched in water, tetrabromocyclopropene is regenerated.

## Vibrational Spectra and Assignments

**Trichlorocyclopropenium Ion.** The infrared spectrum of **6** in the NaCl region, shown in Figure 1A, has just three bands, indicating a highly symmetrical structure. The intense bands characteristic of the parent tetrachlorocyclopropene[9] at 1148, 1055, 753, and 617 $cm^{-1}$ are notably absent. The spectrum of **7** in the same region, as shown in Figure 1B, is essentially *identical* with that of **6**. If molecular adducts[10] or $\pi$ complexes[11] were produced in these reactions it is most unlikely that the spectra of the two products would be so strongly similar or so simple. On the other hand the data are entirely consistent with the formation of trichlorocyclopropenium ion salts.

Observation of spectral bands characteristic for $AlCl_4^-$ in **6** and for $SbCl_5^-$ in **7** provides definite evidence

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[5] S. W. Tobey and R. West, *J. Am. Chem. Soc.*, 88, 2481 (1966).

[6] For a preliminary report of this work see S. W. Tobey and R. West, *ibid.*, 86, 1459 (1964).

[7] Assuming that at equilibrium in a suitable solvent the bromide of **1** would be 99–99.9% ionized according to eq 1, while **5** would be no more than 0.1–1% ionized, we can calculate that substitution of three bromines for phenyls on the cyclopropenium nucleus causes an over-all increase in $\Delta F^\circ$ for ionization of at least 10 kcal, *most* of which would be due to *destabilization* of the tribromocyclopropenium ion relative to **1**.

[8] This unexpected behavior has been observed for other ionic chlorocarbon–aluminum trichloride adducts: H. J. Prins, *Rec. Trav. Chim.*, 51, 1065 (1932), and ref 16.

[9] S. W. Tobey and R. West, *Tetrahedron Letters*, 1179, (1963), and ref 5.

[10] F. M. Rabel and R. West, *J. Am. Chem. Soc.*, 84, 4169 (1962).

[11] H. H. Freedman, *ibid.*, 83, 2194 (1961), and references cited there.

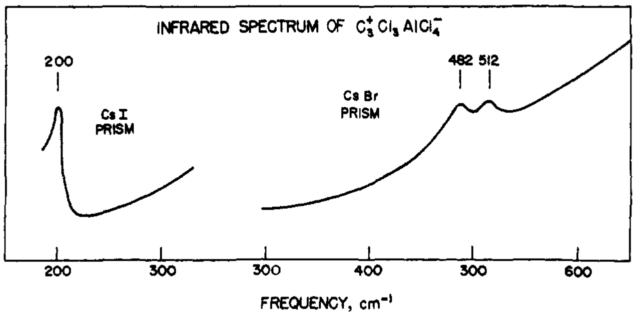

Figure 2. Infrared spectrum of $C_3Cl_3^+AlCl_4^-$ (Nujol mull) long wavelength region.

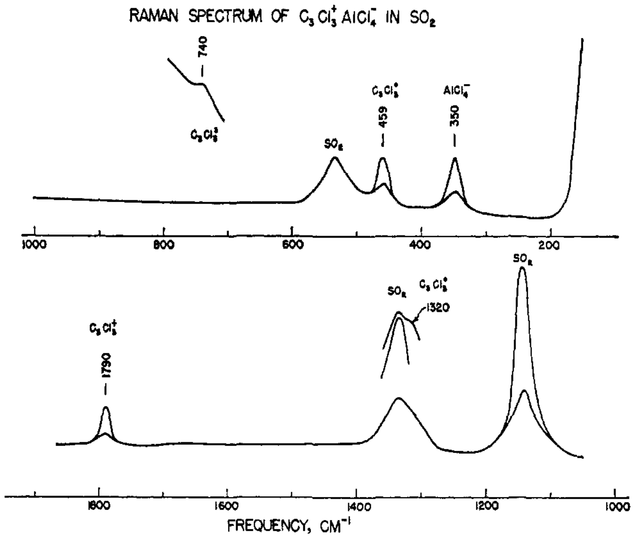

Figure 3. Raman spectrum of $C_3Cl_3^+AlCl_4^-$ in liquid $SO_2$.

for ionic structures for these compounds. The low-frequency infrared spectrum of **6** between 600 and 190 cm$^{-1}$ (Figure 2) shows two closely spaced absorption bands near 490 cm$^{-1}$. The bands are absent in the corresponding spectrum of **7**, which shows instead a broad band at 339 cm$^{-1}$.[12] From these data the band near 490 cm$^{-1}$ should be due to the $AlCl_4^-$ anion. To confirm this prediction the infrared spectra of solid sodium tetrachloroaluminate[13a] and potassium tetrachloroaluminate[13b] were determined. $Na^+AlCl_4^-$ is known from X-ray analysis to be ionic and to contain tetrahedral $AlCl_4^-$ anions.[14] Only one infrared absorption band was observed in the 4000–300-cm$^{-1}$ region for both these compounds, and this appeared at 481 (vs,b) cm$^{-1}$. According to Carlson, absorption due to $AlCl_4^-$ occurs at 490 cm$^{-1}$ in solid $PCl_4^+AlCl_4^-$,[15] and we find it occurring in this same region in other chlorocarbonium ion tetrachloroaluminates.[16] Only a single infrared active Al–Cl stretching band is expected for tetrahedral $AlCl_4^-$; the vibrational doubling in **6** may be a result of crystal field interactions. The Raman spectrum of **6** in liquid sulfur dioxide[17] (Figure 3) provides additional evidence for the ionic structure, for it contains a strong polarized line at 350 cm$^{-1}$ which is diagnostic for $AlCl_4^-$.[15,18]

Elimination of the bands due to the anions from the infrared and Raman spectra leaves four infrared and four Raman absorptions, summarized in Table I. The selection rules for in-plane vibrational modes of $C_3Cl_3^+$, assuming a planar structure with $D_3h$ symmetry,[19] are also shown in Table I. The agreement of the numbers of fundamentals with those predicted, and particularly the lack of coincidence between polarized Raman lines and infrared bands, confirms the $D_3h$ symmetry expected for the trichlorocyclopropenium ion.

**Table I.** Comparison of the Infrared and Raman Spectra of the Trichlorocyclopropenium Ion with That Predicted for a $C_3X_3$ System Having $D_{3h}$ Symmetry

| Predicted spectrum | | | Obsd spectrum | |
|---|---|---|---|---|
| Species | No. | Activity | Raman, freq (cm$^{-1}$) | Infrared, freq (cm$^{-1}$) |
| $A_1'$ | 2 | Raman (pol) | 459 (s, pol)<br>1791 (m, pol) | . . .<br>. . . |
| $E'$ | 3 | Infrared, Raman (dep) | . . .<br>740 (vw)<br>1320 (s, dep) | 200 (s)<br>735 (s)<br>1312 (vs) |
| $A_2''$ | 1 | Infrared (below 200 cm$^{-1}$) | | . . . |
| $E''$ | 1 | Raman (dep, below 100 cm$^{-1}$) | . . . | |
| Unassigned | | | | 1348 (s) |

Two fundamentals of $A_1$ species are predicted, which should be inactive in the infrared but should give rise to polarized Raman lines. Only two strongly polarized Raman lines were observed in the spectrum of $C_3Cl_3^+$, at 459 and 1790 cm$^{-1}$, neither one coincident with an infrared absorption. These lines can therefore confidently be assigned to the $A_1$ modes.

Three fundamentals of E1 species are expected, which should each give rise to a coincident infrared band and depolarized Raman line. The strong infrared bands at 1320 and 740 cm$^{-1}$, coincident with depolarized Raman lines, can therefore be assigned as E1 fundamentals. The remaining infrared band at 200 cm$^{-1}$ was also assigned to this species as a C–Cl bending mode. (A Raman line at this frequency would not be observable under the conditions used because of proximity to the exciting line.) An infrared active mode of $A_2''$ type and an $E''$ Raman line are also predicted, but are expected to lie at frequencies too low to be observed.

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(12) $KSbCl_6$ shows only one infrared band above 300 cm$^{-1}$, at 335 cm$^{-1}$. The $SbCl_6^-$ ion has $O_h$ symmetry and should have two low-frequency infrared active fundamentals. Apparently one lies below 300 cm$^{-1}$; see K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 118, 119.

(13) (a) H. Gerding and H. Houtgraaf, *Rec. Trav. Chim.*, **72**, 21 (1953); (b) H. Friedman and H. Taube, *J. Am. Chem. Soc.*, **72**, 2236 (1950).

(14) N. C. Baenziger, *Acta Cryst.*, **4**, 216 (1951).

(15) G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

(16) R. West and P. Kwitowski, *J. Am. Chem. Soc.*, in press.

(17) Although **6** and **7** are chemically highly reactive, vigorously attacking most solvents in which they are soluble, a relatively stable 30% by weight solution of **6** in liquid $SO_2$ can be made simply by mixing stoichiometric amounts of **4** and aluminum chloride in this solvent. Unfortunately **7** is insoluble in liquid $SO_2$ and no other solvent suitable for Raman spectral studies has yet been found.

(18) The Raman spectrum of $K^+AlCl_4^-$[13b] in $SO_2$ shows just one band in addition to those characteristic of the solvent, and this is a strong, polarized band at 351 cm$^{-1}$. Our experiments on $Na^+AlCl_4^-$ confirm this assignment.

(19) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Inc., New York, N. Y., 1945, Tables 36 and 55, pp 138 and 252, and p 91.

One additional absorption appears in the infrared spectrum of **6** and **7**. This is a band of moderate strength at 1348 cm$^{-1}$, quite close to the intense E′ mode at 1312 cm$^{-1}$. The origin of this band is not certain, but since it is absent in the Raman spectrum it is unlikely to be a $C_3Cl_3^+$ fundamental. The 1348-cm$^{-1}$ band may result from vibrational doubling due to the crystal field in the solid, as suggested for the doublet Al–Cl stretching mode in **6**.

**Tribromocyclopropenium Ion.** Because no suitable solvent for **8** could be found, the spectrum of this compound was studied only in the infrared. Three infrared bands are found, of which a strong broad band at 400 cm$^{-1}$ can be assigned to tetrabromoaluminate ion. (Sodium tetrabromoaluminate, prepared for comparison, shows only one strong absorption band at 401 cm$^{-1}$.) The other two absorptions at 1276 and 575 cm$^{-1}$ are assigned to E′ modes of $C_3Br_3^+$.

The 1276-cm$^{-1}$ band in the infrared spectrum of **8** is very similar to the 1312-cm$^{-1}$ E′ bands found for **6** and **7**. One contributor to the E′ mode of **7** located near 1300 cm$^{-1}$ which has a simple physical interpretation is shown in Figure 4. Note that in this mode only synchronous movement of the CX groups is involved. The net result of these motions is mostly C–C expansion and compression within the ring. The position of the resulting absorption should therefore be affected only slightly by the nature of the substituents, heavier substituents lowering the frequency. The observed E′ frequencies of $C_3Cl_3^+$ and $C_3Br_3^+$ are in accord with this prediction. In their investigations of alkyl- and arylcyclopropenium ions Breslow and his co-workers[4c] and Chatt and Guy[20] note the consistent occurrence of an intense infrared absorption between 1400 and 1430 cm$^{-1}$, which is probably similar to the $C_3X_3^+$ E′ mode.

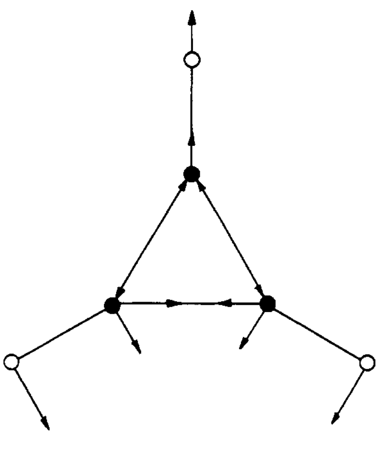

Figure 4. E′ mode of $C_3X_3^+$ which involves mostly C–C stretching.

## Normal Coordinate Analyses

**Trichlorocyclopropenium Ion.** Normal coordinate analysis of the fundamental vibrations of $C_3Cl_3^+$ was carried out using both a simple valence force field (SVFF) and the Urey–Bradley force field (UBFF). The standard G–F matrix method was employed; details are given in the Experimental Section.

Force constants resulting from the normal coordinate analyses are summarized in Table II. The SVFF treatment of $C_3Cl_3^+$ gives a value for the C–Cl stretching force constant of 6.1 mdynes/A, which seems unreasonably high. Chlorinated benzenes, under the same approximation, give $K_{CCl} = 3.8$ mdynes/A.[21] The values for $H_{CCC}$ and $H_{CCl}$ also seem too large using the SVFF approximation. In the SVFF treatment no account is taken of repulsions between chlorine and nonadjacent carbons, which may be substantial in the $C_3Cl_3^+$ ion. We conclude that the SVFF is not a very satisfactory model for $C_3Cl_3^+$, and that better results should be obtained using the UBFF, which should in any case be used to determine constants for comparison with other aromatic species.

In the UBFF, however, there are six constants: two each of stretching, bending, and nonbonding interaction constants. Because only five frequencies could be observed, one constant must be assumed to give a unique solution. Shimanouchi and his co-workers[22] have shown that the nonbonded interaction between chlorine atoms falls off to zero at distances greater than 3.5 A. The nonbonded chlorine atoms in the trichlorocyclopropenium ion should be at least 4.5 A apart and so the interaction constant between them should be zero. Nevertheless, calculations assuming a small positive value of 0.08 mdyne/A for $C_{ClCl}$, as well as a zero value, were carried out (Table II). Introduction of a nonzero value for $C_{ClCl}$ gives less reasonable values for the other constants (particularly for $K_{CCl}$). The zero value for $C_{ClCl}$ is therefore preferred, consistent with the results of Shimanouchi.[22]

**Table II.** Force Constants for $C_3X_3^{+a}$

| | $C_3Cl_3^+$ | | | $C_3Br_3^+$ | |
|---|---|---|---|---|---|
| | SVFF | UBFF | | UBFF | |
| $K_{CC}$ | 5.30 | 6.31 | 6.74 | 6.46 | 6.46 |
| $K_{CX}$ | 6.14 | 2.99 | 5.08 | 2.15 | 2.27 |
| $H_{CCC}$ | −0.447 | −0.248 | −0.497 | (−0.248) | (−0.248) |
| $H_{CCCl}$ | −0.711 | 0.385 | 0.996 | (0.275) | (0.275) |
| $F_{CCl}$ | . . . | 0.808 | −0.145 | (0.674) | (0.624) |
| $C_{ClCl}$ | . . . | (0.00) | (0.08) | (0.00) | (0.00) |

[a] Values listed in parentheses are estimated.

Under the UBFF approximation, a value of 2.99 mdynes/A is found for $K_{CCl}$ (Table II). This is large compared to the value observed for chlorobenzenes under the same approximation (~1.9 mdynes/A)[21] but satisfactorily close to the value of 2.66 found for tetrachloroethylene.[23] The unit positive charge present on $C_3Cl_3^+$ should tighten the bonding between C and Cl somewhat. The C–C–C bending force constant is found to have a small negative value. Saksena has also found a negative value for $H_{C-C-C}$ in cyclopropane.[24] We believe that a negative sign for $H_{CCC}$ is not unreasonable for highly strained molecules such as three-membered rings, but further interpretation would be speculative in the absence of knowledge about the generality of this effect. The value of $K_{CC}$ is discussed in the following section of this paper.

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(20) J. Chatt and R. G. Guy, *Chem. Ind.* (London), 212 (1963).

(21) J. R. Scherer, *Spectrochim. Acta*, 20, 345 (1964).

(22) T. Hiraishi, I. Nakagawa, and T. Shimanouchi, *ibid.*, 20, 819 (1964).

(23) D. E. Mann, T. Shimanouchi, J. H. Meal, and L. Fano, *J. Chem. Phys.*, 27, 43 (1957).

(24) B. D. Saksena, *Proc. Indian Acad. Sci.*, 10*A*, 449 (1939).

**Tribromocyclopropenium Ion.** A complete normal coordinate analysis is not possible because only two fundamentals were observed. These fundamentals are presumed to be mainly C–C and C–Br stretching frequencies, and so they were used to calculate values of $K_{CC}$ and $K_{CBr}$, as a check on the results of the $C_3Cl_3^+$ analysis. The other necessary force constants were estimated from those obtained for $C_3Cl_3^+$ by making the following assumptions: (1) the C–C–C bending constant, $H_{CCC}$, is the same as that for $C_3Cl_3^+$, and (2) the ratios $H_{CCCl}/H_{CCBr}$ and $F_{CCl}/F_{CBr}$ for $C_3Cl_3^+$ and $C_3Br_3^+$ are equal to the ratio of force constants of the same kind taken from other chloro and bromo hydrocarbons. Two values for each ratio were determined, using data from aliphatic halo compounds[25] and from tetrahaloethylenes.[23] The force constants $K_{CC}$ and $K_{CBr}$ obtained under these approximations are given as the fourth and fifth columns of Table II. $K_{CC}$ for $C_3Br_3^+$ is in good agreement with that for $C_3Cl_3^+$, and the ratio $K_{CCl}/K_{CBr}$ is reasonable.

## Discussion of Results

The most important result of the UBFF calculations is the unusually large C–C stretching force constant in $C_3Cl_3^+$. C–C stretching force constants calculated for a number of aromatic species under the Urey–Bradley approximation are shown in Table III. Scherer and Overend[26] have calculated $K_{CC}$ for benzene; the value depends somewhat on the value chosen for the resonance constant $\rho$, but lies between 5.2 and 5.6 mdynes/A. In a previous study we found that the C–C stretching force constant for cyclopentadienide ion has a similar value.[27] The constant $K_{CC}$ for hexachlorobenzene is somewhat lower, as is reasonable because of the inductive effect of the chlorines, but is also close to 5 mdynes/A. The C–C stretching force constant in $C_3Cl_3^+$, 6.3 mdynes/A, is markedly larger than that for the five- and six-membered aromatic rings.

Table III. Urey–Bradley Force Constants for Aromatic Species (in Mdynes/A)

| | $K_{CC}$ | $K_{CX}$ | $\rho$ | Ref |
|---|---|---|---|---|
| $C_6H_6$ | 5.59 | 4.76 | 0 | 26 |
| | 5.15 | 4.79 | 0.35 | 26 |
| $C_5H_5^-$ | 5.39 | 4.79 | 0.21 | 27 |
| $C_6Cl_6$ | 4.81 | 2.30 | 0.366 | 22 |
| $C_3Cl_3^+$ | 6.32 | 2.99 | 0 | *a* |
| $C_3Br_3^+$ | 6.46 | 2.2 | 0 | *a* |

[a] Present work.

The reason for the exceptionally high value for $K_{CC}$ in $C_3Cl_3^+$ is not yet fully understood, but it may be associated with an unusually short C–C distance in the ion. Sundaralingham has recently found that in triphenylcyclopropenium perchlorate, the C–C bond distance in the ring is only 1.373 ± 0.005 A, significantly *shorter* than the C–C bond distance in benzene.[28] Thus both the structural and spectroscopic evidence confirm the strongly aromatic character predicted for cyclopropenium ions. Simple Hückel molecular orbital calculations predict a resonance energy of 2.00$\beta$ and a bond order of 1.667 for the unsubstituted $C_3H_3^+$ ion,[2] just the same values as for benzene. These calculations of course do not consider the decreased electron repulsion due to the positive charge in $C_3H_3^+$ which should change particularly the coulomb integral $\alpha$. An SCF calculation taking explicit account of electron repulsions might give a higher bond order for a cyclopropenium species, but such a calculation for $C_3Cl_3^+$ is too formidable to be attempted at present.

The high C–C bond strength in $C_3Cl_3^+$ implied by the stretching force constant is all the more remarkable considering that the C–C $\sigma$ bonds in the three-membered ring must be strongly bent, and presumably weaker than in benzene. If the C–C distance is unusually short in $C_3Cl_3^+$, the reduction in $\sigma$ bond strength is evidently more than compensated for by increased $\pi$ bonding. Overlap of the carbon p orbitals undoubtedly increases with decreasing C–C distance. A further implication of these conclusions is that in conventional aromatic species such as benzene, the limitation on approach of adjacent carbon atoms, and so on $\pi$ overlap, may result from repulsive interactions involving $\sigma$-bonding electrons. When the $\sigma$ framework is strongly bent, as in $C_3Cl_3^+$, the repulsions may be decreased with consequent shortening of the C–C distance and increased $\pi$ bonding.

## Experimental Section

The Lewis acid adducts were prepared using purified grades of commercially available metal halides. The $SO_2$ was Matheson 99.95% anhydrous grade. Elemental analyses were performed in the Microanalytical Laboratory of Dr. Alfred Bernhardt, Mulheim/Ruhr, Germany. Gas chromatographic analyses were performed at 120–160° on a Wilkins Aerograph A-90 thermoconductivity detector instrument using He carrier and a 5 ft × 0.5 in. column packed with 20% G.E. SF-96 on 30–60 mesh firebrick. Raman spectra were recorded on a Cary Model 81 spectrometer using the Hg 4358-A exciting line. The samples were contained in standard wall 7 mm o.d. × 24 cm sealed Pyrex cells with 12 mm o.d. blown bulbous front windows. Infrared spectra in the 4000–625-$cm^{-1}$ region were obtained on Nujol or fluorocarbon oil mulls between NaCl plates using Perkin-Elmer Model 237 and Model 421 spectrometers. Infrared spectra in the 650–180-$cm^{-1}$ region were taken between CsI plates or polyethylene films on a Perkin-Elmer Model 112 single-beam recording spectrometer equipped with a CsBr or CsI prism. Band positions were assigned from a predetermined calibration curve. Listed infrared frequencies are correct to $\pm 2$ $cm^{-1}$.

**Trichlorocyclopropenium Tetrachloroaluminate (6).** Anhydrous $AlCl_3$ powder (0.51 g, 0.0038 mole) was mixed with 2 ml of tetrachlorocyclopropene under $N_2$. The mixture was agitated, and then spot-warmed momentarily. A mildly exothermic reaction started at the point of warming and spread gradually through the mixture, turning it pale tan. When this reaction had ceased, excess tetrachlorocyclopropene was immediately removed by pumping for 15 min at 0.02 mm. A pale tan, amorphous powder remained which weighed 1.21 g, corresponding to the uptake of 0.70 g (0.0039 mole) of tetrachlorocyclopropene and the formation of a 1:1 complex (**6**).

*Anal.* Calcd for $C_3Cl_4 \cdot AlCl_3$: C, 11.59; H, 0.00; Cl, 79.72; Al, 8.69. Found: C, 11.48; H, 0.09; Cl, 79.61; Al, 8.80.

Compound **6** gradually turned dark brown and pasty when heated above 150° and a colorless liquid distilled off. Infrared analysis of this liquid showed that it was tetrachlorocyclopropene.[5] On pouring 1 g of **6** into 5 ml of water, a vigorous reaction occurred and 0.2 ml of light tan oil was thrown down.[8] This oil was drawn off, dried over a granule of $CaCl_2$, and subjected to gas chromatographic analysis. Only one peak was eluted. On infrared analysis it proved to be tetrachlorocyclopropene.

**Trichlorocyclopropenium Tetrachloroaluminate (6). Preparation in Liquid Sulfur Dioxide.** Anhydrous $AlCl_3$ powder (3.30 g,

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0.0247 mole) in a Pyrex tube was cooled to −78° in $CO_2$–acetone under $N_2$. Ten milliliters of liquid $SO_2$ was added. The tube was warmed almost to −10° and the contents was stirred with a nickel spatula. Approximately half the $AlCl_3$ remained undissolved. The tube was recooled and tetrachlorocyclopropene (4.25 g, 0.0239 mole) was added dropwise. On mixing and warming toward −10° a pale yellow solution was obtained over a very small amount of undissolved $AlCl_3$ and alumina. The solution was allowed to stand at −20° until it settled, and most of the clear supernatant solution was decanted into a second tube cooled to −78°. On standing, copious amounts of well-formed white crystals deposited in this tube. These crystals were filtered off rapidly under $N_2$ on a sintered-glass filter funnel precooled in $CO_2$, and then allowed to warm to room temperature under $SO_2$ vapor; 2.61 g (35% yield) of snow white crystals of **6**, mp 157–159° (sealed tube), were obtained. This material remained snow white for several weeks in sealed tubes. The Nujol mull infrared spectrum of **6** prepared in $SO_2$ was identical with that of **6** prepared as described above.

**Raman Spectrum of Trichlorocyclopropenium Tetrachloroaluminate (6) in Liquid Sulfur Dioxide.** Two grams of $C_3Cl_3^+AlCl_4^-$ crystallized from $SO_2$ was placed in a special Pyrex Raman tube described above. After cooling in crushed $CO_2$, 4.67 g of $SO_2$ was distilled in and the tube sealed off at the rear. The Raman spectrum of the resulting colorless 30% by weight solution is shown in Figure 3.[29] Pure $SO_2$ run under identical conditions showed lines at 527 (m, dep), 1091 (vw), 1146 (vs, pol), and 1332 (vs, dep) $cm^{-1}$.[30]

**Trichlorocyclopropenium Hexachloroantimonate (7).** One milliliter of $SbCl_5$ and 1.0 ml of tetrachlorocyclopropene were mixed under $N_2$. A creamy white paste formed which after standing a few seconds became warm and set to a firm mass. This material was pumped down to 0.05 mm for 1 hr leaving a creamy white, amorphous powder (**7**). The Nujol mull infrared spectrum of **7** in the NaCl region is shown in Figure 1B. **7** attacked CsI rapidly, turning it orange, but a good, low-frequency infrared spectrum was obtained between polyethylene films.[31] A few specks of **7** dropped into liquid $SO_2$ just below −10° failed to dissolve on stirring. When 1 drop of $C_3Cl_4$ was added to 5 ml of liquid $SO_2$ at −20° containing 5 drops of $SbCl_5$, a white precipitate of **7** was thrown down immediately. When quenched in water or heated dry, **7** liberated $C_3Cl_4$.

*Anal.* Calcd for $C_3Cl_4 \cdot SbCl_5$: C, 7.55; Sb, 25.50; Cl, 66.95. Found: C, 7.40; Sb, 26.6; Cl, 66.0.

**$C_3Cl_4 \cdot FeCl_3$.** Two milliliters of tetrachlorocyclopropene was added to 0.5 g of black, crystalline $FeCl_3$ under $N_2$. On momentary warming the $FeCl_3$ crystals disintegrated forming a light tan suspension. Evaporation of excess tetrachlorocyclopropene at 0.05 mm left a tan, amorphous powder. The Nujol mull infrared spectrum of this material in the NaCl region showed bands at 732 (s,s), 1313 (vs,b), and 1346 (s,s) $cm^{-1}$, thus indicating the presence of $C_3Cl_3^+$ ion.

*Anal.* Calcd for $C_3Cl_4 \cdot FeCl_3$: C, 10.59; H, 0.00; Fe, 16.41; Cl, 73.00. Found: C, 10.53; H, 0.22; Fe, 16.5; Cl, 73.14.

**$C_3Cl_4 \cdot GaCl_3$.** Ten grams (0.056 mole) of gallium chloride was dissolved in 50 ml of liquid sulfur dioxide at −70° under a nitrogen atmosphere. Tetrachlorocyclopropene (10.0 g, 0.056 mole) was added slowly from a dropping funnel. No immediate precipitation took place. The mixture was allowed to warm and excess sulfur dioxide was removed in a stream of nitrogen. Long, white needles slowly formed in the solution. After most of the excess $SO_2$ had been evaporated, 50 ml of dichloromethane was added and the slurry was filtered under nitrogen. The product, a colorless, crystalline solid, was washed with dichloromethane and dried under vacuum.

*Anal.* Calcd for $C_3Cl_4 \cdot GaCl_3$: C, 10.2; Cl, 70.5; Ga, 19.7. Found: C, 11.0; Cl, 68.3; Ga, 20.8.

**Sodium Tetrachloroaluminate. Infrared Spectrum.** Sodium chloride (1.07 g, 0.020 mole) and aluminum chloride (2.67 g, 0.020 mole) were mixed in a Pyrex tube under $N_2$ then heated to 250°.[13a] A gray liquid over a small amount of undissolved NaCl resulted. A portion of the supernatant melt was decanted into another tube and allowed to solidify. The Nujol mull infrared spectrum of the solid $Na^+AlCl_4^-$ in the region 2000–300 $cm^{-1}$ showed just one peak at 481 (vs,vb) $cm^{-1}$. The $Na^+AlCl_4^-$ was found to be essentially insoluble in liquid $SO_2$.

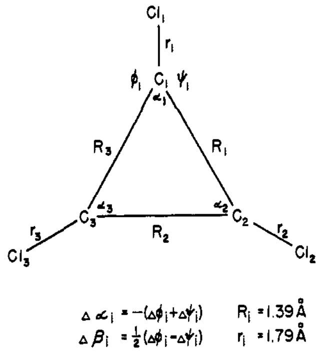

Figure 5. Internal coordinates for $C_3Cl_3^+$.

**Potassium Tetrachloroaluminate. Infrared and Raman Spectra.** A mixture of KCl (2.95 g, 0.0395 mole) and $AlCl_3$ (5.28 g, 0.0395 mole) was heated under $N_2$ in a Pyrex tube. A tan liquid over a small amount of unreacted KCl resulted. A portion of the melt was decanted off and cooled.[13b] The infrared spectrum of this solid $K^+AlCl_4^-$ showed just one peak at 482 (vs,vb) $cm^{-1}$ in the region 4000–300 $cm^{-1}$ (Nujol mull). Some of this solid (1.43 g) was sealed in a Pyrex Raman tube of the type described earlier with 5.66 g of $SO_2$. At room temperature only a very small amount of the salt failed to dissolve. The Raman spectrum of this 20% by weight (saturated) solution showed bands characteristic of the solvent, plus one additional very strong polarized band at 351 $cm^{-1}$.

**Tribromocyclopropenium Tetrabromoaluminate (8).** Aluminum bromide (0.85 g, 0.0032 mole) was dissolved in 5 ml of $CS_2$, and tetrabromocyclopropene[5] (1.10 g, 0.0031 mole) was added dropwise. A light tan precipitate formed immediately which was filtered off on a sintered glass funnel under $N_2$. After drying under vacuum, the precipitated **8** weighed 1.85 g, suggesting it was a 1:1 adduct. On quenching in water **8** provided a tan oil which on gas chromatographic work-up proved to be tetrabromocyclopropene by infrared analysis.

*Anal.* Calcd for $C_3Br_4 \cdot AlBr_3$: C, 5.79; H, 0.00; Al, 4.34; Br, 89.88. Found: C, 5.74; H, 0.21; Al, 4.50; Br, 89.91.

## Normal Coordinate Analysis

Internal coordinates used in the calculation are similar to those given in a previous paper;[32] they are shown in Figure 5. The set of internal symmetry coordinates, constructed for D₃h symmetry, is as follows.

$$S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3) \qquad (A_1')$$

$$S_2 = \frac{1}{\sqrt{3}}(\Delta R_1 + \Delta R_2 + \Delta R_3)$$

$$S_3 = \frac{1}{\sqrt{3}}(r\Delta\beta_1 + r\Delta\beta_2) + r\Delta\beta_3) \qquad (A_2')$$

$$S_{4a} = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_3) \qquad (E')$$

$$S_{5a} = \frac{1}{\sqrt{6}}(2r\Delta\beta_1 - r\Delta\beta_2 - \Delta\tau\beta_3)$$

$$S_{6a} = \frac{1}{2\sqrt{2}}(\Delta R_1 - \Delta R_3) - \frac{\sqrt{3}}{2\sqrt{2}}(R\Delta\alpha_2 - R\Delta\alpha_3)$$

The potential energy can be expressed in the following form for SVFF

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[29] This solution turned yellow and then orange on standing for 2 weeks at room temperature. At 25° the internal pressure in the Raman tubes is over 5 atm so that the tubes should be handled with caution. During the Raman experiment a steady flow of cool air was forced over the Raman tube so that its temperature never exceeded 25°.

[30] G. Herzberg, ref 19, p 285.

[31] I. Cohen, *J. Chem. Educ.*, **39**, 262, 595 (1962).

[32] M. Ito and R. West, *J. Am. Chem. Soc.*, **85**, 2580 (1963).

$$2V_{\text{SVFF}} = \sum_{i=1}^{3} K_{\text{CC}}\Delta R_i{}^2 + \sum_{i=1}^{3} k_{\text{CX}}\Delta r_i{}^2 + \sum_{i=1}^{3} H_{\text{CCC}}(R\Delta\alpha_i)^2 + \sum_{i=1}^{3} {}^3H_{\text{CCX}}(r\Delta\beta_i)^2$$

and for UBFF

$$2V_{\text{UBFF}} = 2V_{\text{SVFF}} + 2\sum_{i=1}^{3} K_{\text{CC}}{}'R\Delta R_i + 2\sum_{i=1}^{3} K_{\text{CX}}{}'r\Delta r_i + 2\sum_{i=1}^{3} H_{\text{CCX}}{}'r^3\Delta\beta_i + \sum_{i=1}^{3} F_{\text{CX}}[(\Delta q_{\text{C}_i\text{X}_{i+1}})^2 + (\Delta q_{\text{C}_i\text{X}_{i-1}})^2] + 2\sum_{i=1}^{3} F_{\text{CX}}{}'[q_{\text{CX}}(\Delta q_{\text{C}_i\text{X}_{i+1}} + \Delta q_{\text{C}_i\text{X}_{i-1}})] + \sum_{i=1}^{3} C_{\text{XX}}(\Delta q_{\text{X}_i\text{X}_{i+1}})^2 + 2\sum_{i=1}^{3} C_{\text{XX}}{}'(q_{\text{XX}}\Delta q_{\text{X}_i\text{X}_{i+1}})$$

where *K* and *H* have their usual meanings of stretching and bending force constants, respectively, X denoting halogen. $F_{\text{CX}}$ and $C_{\text{XX}}$ are geminal and *cis* repulsion terms, respectively, between nonbonded atoms; *q* is the distance between nonbonded atoms. The linear terms are indicated with a prime.

In the calculation the usual assumption was made that the linear terms are −0.1 of the corresponding quadratic terms. Bond lengths are not available for these ions, and so distances $R_{\text{CC}} = 1.39$ A, $\gamma_{\text{CCl}} = 1.79$ A, and $r_{\text{CBr}} = 1.90$ A were assumed. Force constants were refined by iterative calculation using a Consolidated Data Corp. 1604 electronic digital computer.

In the SVFF calculation, the observed frequencies were all equally weighted except for the band at 200 cm$^{-1}$, which was given a weighting one-half as large as the others. The agreement of the calculated and observed frequencies were within ±0.4% except for the 200-cm$^{-1}$ band, which showed a deviation of −5.1%.

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# Thermally Induced Skeletal Rearrangements of Tropilidenes[1]

**Jerome A. Berson and M. Robert Willcott, III**[2]

*Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin.* *Received February 4, 1966*

**Abstract:** 3,7,7-Trimethyltropilidene heated at 300° in the gas phase gives a mixture containing recovered starting material, 2,7,7- and 1,7,7-trimethyltropilidenes, 3- and 6-isopropenyl-1-methyl-1,4-cyclohexadienes, and *m*- and *p*-cymenes. The nonaromatizing rearrangements are reversible. Under the same conditions, 1,5-dideuterio-3,7,7-trimethyltropilidene gives the corresponding dideuterated products, in each of which the alternating pattern (D, H, lone methyl, H, D) of substitution characteristic of the starting material is preserved. The rearrangement is therefore one in which the carbons 1–6 of the starting material remain in the same sequence, while C-7 and its geminal methyls are allowed to wander and reattach between any adjacent pair.

Tropilidene (**1**) is perhaps the most intensively studied member of the class of odd-numbered cyclic polyenes $CH_2(CH{=}CH)_n$ (*n* = 1, 2, . . . . .). Its response to thermal energies over the temperature range from −150 to above 400° has been examined by a variety of techniques. The most facile change is the conformational ring inversion (*e.g.*, **1a** ⇌ **1b**) of two nonplanar isomers revealed by the low-temperature nmr spectrum of the parent compound ($E_a$ = 5.7–6.3 kcal/mole)[3] and the 2-*t*-butyl-3,7,7-trimethyl derivative.[4] At a perhaps slightly higher level of activation energy may lie the much discussed[5–8] cycloheptatriene–norcaradiene (**2**) interconversion. From bond-energy tables, a rough value of 11 ± 4 kcal/mole is calculated[9] for the endothermicity and hence for the minimum activation energy of the **1** → **2** reaction. In the range of temperatures high enough to overcome an activation energy of about 31 kcal/mole, the hydrogens of tropilidene spread over the carbon framework by successive C-7 → C-3 jumps, as is observed in the behavior of 7-deuterated derivatives.[10a] This epidermal rearrangement

**1a** **1b**

**1** **2**

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[1] (a) We are indebted to the Camille and Henry Dreyfus Fund and to the Army Research Office (Durham) for support of this work. (b) For preliminary reports, see J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, 87, 2751, 2752 (1965).

[2] National Institutes of Health Postdoctoral Fellow, 1964–1965.

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[5] *Cf.* W. von E. Doering and M. R. Willcott, III, *Tetrahedron Letters*, 663 (1962), and references cited therein for earlier literature.

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[9] W. von E. Doering and M. R. Willcott, III, unpublished; M. R. Willcott, III, Ph.D. Dissertation, Yale University, 1963.