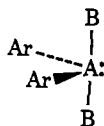


Additional observations which are consistent with these ideas are provided by studies of other hyper-valent derivatives of group VI elements of the general type Ar_2AB_2 (7). The $Ar-A-Ar(C-A-C)$ angles in



7

$(p-CH_3C_6H_4)_2SeCl_2$ and $(p-CH_3C_6H_4)_2SeBr_2$ are $106.5(1.0)$ and $108(1)^\circ$,⁵⁰ respectively, while in $(C_6H_5)_2-$

$TeBr_2$,⁵¹ and $(p-ClC_6H_4)_2TeI_2$,⁵² they are $96.3(1.2)$ and $101.1(1.0)^\circ$. The more electronegative the B ligand the smaller the $C-A-C$ angle as long as A is constant. The variation in $C-A-C$ angles ($S > Se > Te$) as A is changed is that predicted by the rule given by Bent.⁴⁵

Acknowledgment. We thank the U. S. National Science Foundation for partial support of this research through grant number GP 13339.

(50) J. D. McCullough and R. E. Marsh, *Acta Crystallogr.*, **3**, 41 (1950).

(51) G. D. Christofferson and J. D. McCullough, *ibid.*, **11**, 249 (1958).

(52) G. Y. Chao and J. D. McCullough, *ibid.*, **15**, 887 (1962).

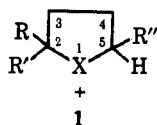
Synthesis of Substituted Five-Membered Ring Halonium Ions and Their Reactions with Nucleophiles

Paul E. Peterson*¹ and Benedict R. Bonazza²

Contribution from the Department of Chemistry, St. Louis University, St. Louis, Missouri 63156. Received December 11, 1971

Abstract: 3-Chlorotetramethylene-, 3-methyltetramethylene-, *cis*-cyclohexane-1,2-dimethylene-, *cis*-3,4-dichlorotetramethylenechloronium, and 3-bromotetramethylenebromonium ions were formed by ionization of 1,2,4-trichlorobutane, 1,4-dichloro-2-methylbutane, *cis*-1,2-bis(chloromethyl)cyclohexane, *meso*-1,2,3,4-tetrachlorobutane, and 1,2,4-tribromobutane, respectively, in antimony pentafluoride-sulfur dioxide solution at -65 to -78° . Reaction of 3-chloro- and 3-methyltetramethylenechloronium ions with dimethyl ether, methanol, acetic acid, and trifluoroacetic acid in each case gave the expected two products whose ratio is presumed to reflect the steric and inductive effects of the substituent.

In previous investigations³⁻⁵ it has been shown that cyclic five-membered ring halonium ions can be prepared by the ionization of 1,4-dihaloalkanes in antimony pentafluoride-sulfur dioxide at low temperatures. Depending on the starting alkane various alkyl and/or haloalkyl substituents can be incorporated into the ring structure 1.



The first five-membered ring ions prepared were the tetramethylene- (unsubstituted, $R = R' = R'' = H$; $X = Cl, Br, I$), 2-methyltetramethylene- (primary-secondary, $R = CH_3$; $R' = R'' = H$; $X = Cl, Br, I$), and the 2,5-dimethyltetramethylene- (disubstituted, $R = R'' = CH_3$; $R' = H$; $X = Cl, Br, I$) halonium ions.³ Reaction of the 2-methyltetramethylenehalonium ions with methanol gave secondary ether products, indicating the preference for SN_1 type ring opening. The 2,2-dimethyltetramethylenehalonium ions ($R = R' = CH_3$; $R'' = H$; $X = Cl, Br, I$) similarly gave a tertiary ether product⁴ upon reaction with methanol.

(1) Address correspondence to this author at: Chemistry Department, University of South Carolina, Columbia, S. C. 29208.

(2) NDEA Fellow, 1967-1970.

(3) G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968).

(4) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968).

(5) P. E. Peterson, P. R. Clifford, and F. J. Slama, *ibid.*, **92**, 2840 (1970).

Presently the only halo-substituted five-membered halonium ions which have been prepared are the 2-chloromethyltetramethylenechloronium ion ($R = CH_2Cl$; $R' = R'' = H$; $X = Cl$) and the 2-bromomethyltetramethylenebromonium ion ($R = CH_2Br$; $R' = R'' = H$; $X = Br$).⁵ On reaction with methanol, these ions gave ethers derived from both possible ring opening reactions, with the SN_2 like opening product predominating,⁵ in contrast with the results cited above for other ions. This result presumably reflects the inductive influence of the haloalkyl substituent.

The predominantly qualitative results cited above indicate that halonium ion reactions are open for quantitative exploration of the role of such factors as inductive substituent effects, delocalization of charge in transition states, and the effect of reactant nucleophilicity and/or basicity. Such studies are, in part, analogous to those involving solvolytic reactions of substrates such as tosylates, chlorides, and, particularly, sulfonium salts $[R'S(R)_2]^+X^-$. The relatively unstudied chloronium ion substrates, however, possess possibly the most reactive leaving group, $[RCl]^+$, of any compound yet obtained as a stable species, permitting studies of reactions in "inert" solvents (*e.g.*, SO_2) where the influence of reactant nucleophilicity can be studied without concomitant variation of ionizing power. As in solvolytic studies, competition experiments and direct measurement of rates of reaction may be envisioned. The present paper utilizes the former method (competition) to explore the interaction of inductive substituent effects in the halonium ion with the nucleophilic-

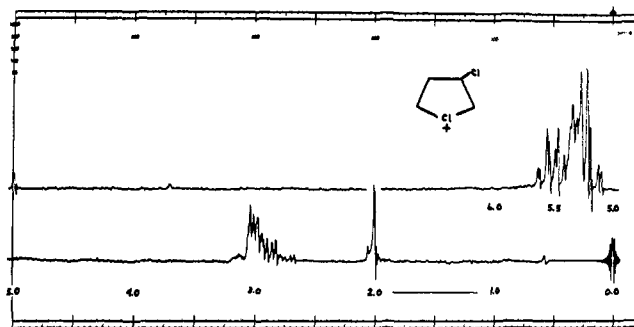
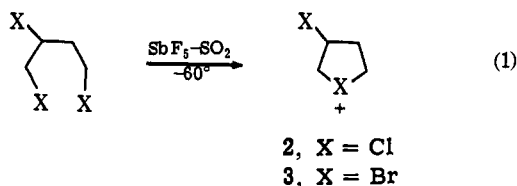


Figure 1. Nmr spectrum (SO_2 , -60° , external TMS capillary: the 3-chlorotetramethylenechloronium ion 2.

ity of the entering group reactant. Related rate studies, undertaken concurrently in our laboratories, are reported in a separate paper.⁶

Synthesis of Ions

When 1,2,4-trichloro- and 1,2,4-tribromobutane were allowed to react with antimony pentafluoride-sulfur dioxide at -60° the 3-chlorotetramethylenechloronium ion 2 and the 3-bromotetramethylenebromonium ion 3, respectively, were obtained (eq 1). The nmr spectrum



of 3 closely resembles that of 2, shown in Figure 1. The nmr data for all the ions to be discussed are summarized in Table I. The singlets at δ 2.0 in Figure 1 are signals

Table I. Proton Magnetic Resonance Data of Tetramethylenehalonium Ions^a

			R'CCH ₂ -X and RCCH ₂ -X	CCH ₂ C	-CH(R)-
R	X	R'			
Cl	Cl	H	5.0-5.7	2.6-3.2	5.0-5.7
Br	Br	H	4.9-5.6	2.7-3.3	4.9-5.6
CH ₃	Cl	H	4.9-5.4	2.1-2.7	2.9-3.2 ^b
Cl	Cl	Cl	5.52		5.27
			5.75		
Ring ^a	Cl	Ring ^a	4.8-5.3		2.9-3.1

^a The ion is 7 of eq 4. ^b δ , CH₃ = 1.17, J = 6.5 Hz.

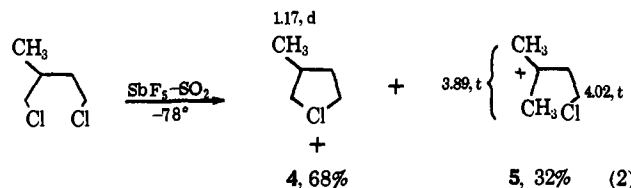
from acetone in the TMS reference capillary. The integrated area of the acetone peak in standardized acetone-TMS capillaries was used to obtain an approximate measure of yields of ions.

The possibility of three-membered ring halonium ion formation exists for the trihalide reactants of eq 1, but can be ruled out based on reactions of the ions (see below). The chemical shift of the downfield hydrogens of 3, δ 4.9-5.3, agrees more closely with that for methylene hydrogens next to positive bromine in the five-

(6) P. E. Peterson and F. J. Waller, *J. Amer. Chem. Soc.*, **94**, 5024 (1972).

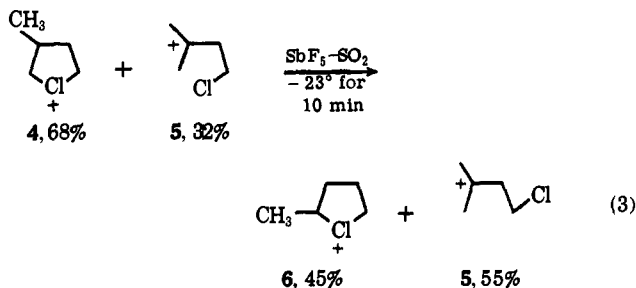
membered tetramethylenebromonium ion, δ 5.20,³ than for the respective protons in the three-membered propylenebromonium ion, δ 5.86.⁷

Reaction of 1,4-dichloro-2-methylbutane with antimony pentafluoride-sulfur dioxide gave a mixture of two species: the 3-methyltetramethylenechloronium ion 4 and tertiary carbonium ion 5, in the relative percentages shown in eq 2. In the nmr spectrum of the



mixture (Figure 2) the distinguishing features of the carbonium ion species 5 are the two triplets for the methylene protons of the CH₂Cl group and the methyl protons at δ 4.02 and 3.89, respectively. The methyl protons appear as a triplet owing to long-range coupling to the nearer methylene protons. The methyl hydrogen chemical shift (δ 3.89) agrees well with that shown by the tertiary amyl cation.⁸ The complex multiplet at δ 5.15 (CH₂Cl⁺) and the methyl doublet at 1.17 (shifted 0.41 ppm downfield from the doublet of the starting dichloride in SO₂ at -60°) are evidence for the presence of the structure 4.

If the antimony pentafluoride-sulfur dioxide solution of 4 and 5 is warmed at -23° for approximately 10 min 4 undergoes an apparent 1,2-methyl shift to give the 2-methyltetramethylenechloronium ion 6 in the relative percentages shown in eq 3. For the reaction of



eq 4, $t_{1/2}$ is approximately 9 min at -40° . Ion 6 has been previously prepared and identified.³ The percentages of eq 3 suggest that 4, on warming, gives hydride shift product 5 along with the methyl shift product 6. The possibility of decomposition of some of 4 to give products undetected by nmr (polymer?) cannot be ruled out, however. Further warming of 5 and 6 for up to 20 min at -23° gives no change in their relative amounts. It is reasonable on grounds of small but appreciable charge delocalization by the methyl substituent in ion 6 that 6, a primary-secondary halonium ion, should be more stable than ion 4, a diprimary ion.

Ionization of *cis*-1,2-bis(chloromethyl)cyclohexane in antimony pentafluoride-sulfur dioxide appeared to give ion 7 (eq 4) along with smaller amounts of other species. Warming the solution containing ion 7 to -10° caused the ion peaks at δ 5.05, attributed to CH₂Cl⁺, to drop in intensity and minor peaks at δ 4.15

(7) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968).

(8) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

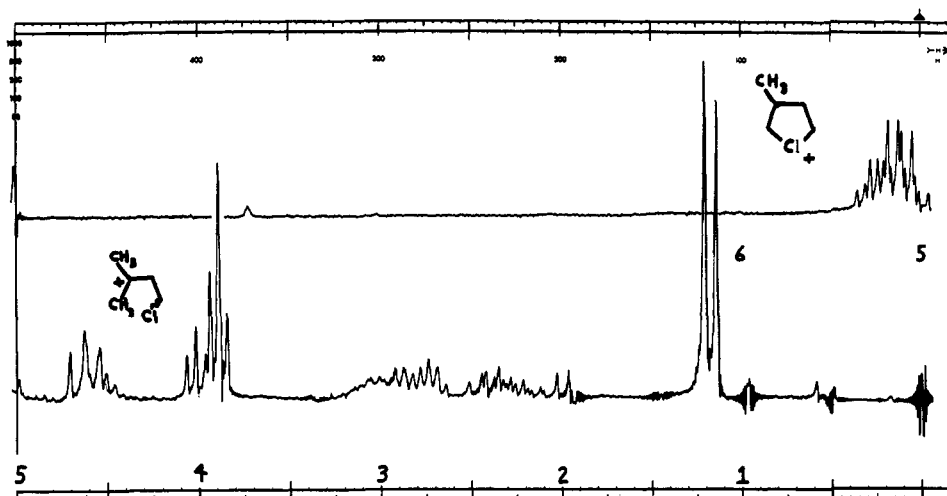
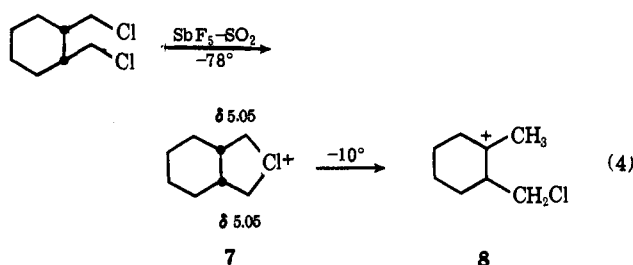


Figure 2. Nmr spectrum (SO_2 , -60° , external TMS capillary): the 3-methyltetramethylenchloronium ion **4** and the 4-chloro-2-methyl-2-butyl cation **5**.



and 3.50 to grow into major peaks. Although the resulting spectrum was not fully interpreted, analogy with the hydride shift reaction of eq 3 suggests **8** as a possible product (eq 4).

When *meso*-1,2,3,4-tetrachlorobutane was ionized in antimony pentafluoride-sulfur dioxide solution at -23° for approximately 1.5 hr or at 0° for 1 min the *cis*-4,5-dichlorotetramethylenchloronium ion **9** was obtained (eq 5). The nmr spectrum of **9**, shown in

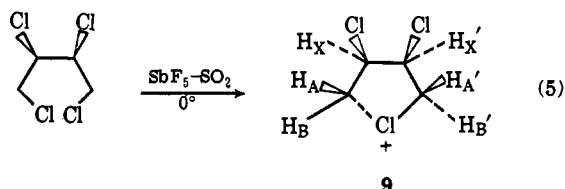


Figure 3, would be a simple ABX system if no coupling existed between the two methine hydrogens. Such coupling could lead to the complex ABXA'B'X' type of spectrum which may be described as showing virtual coupling.⁹ A detailed study of the ^1H and ^{13}C spectra of the ions reported in this paper is in progress. It is of interest that *cis*-1,2,3,4-tetrachlorobutane failed to react at an appreciable rate with $\text{SbF}_5\text{-SO}_2$ at -60° . This diminished reactivity may be due to the inductive effect of the β chlorine atoms which should impede abstraction of a chloride ion relative to 1,4-dichlorobutane.

Reactions of Ions with Nucleophiles

Ions **4** (admixed with **5**) and **2** were allowed to react with methanol, dimethyl ether, acetic acid, and tri-

(9) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

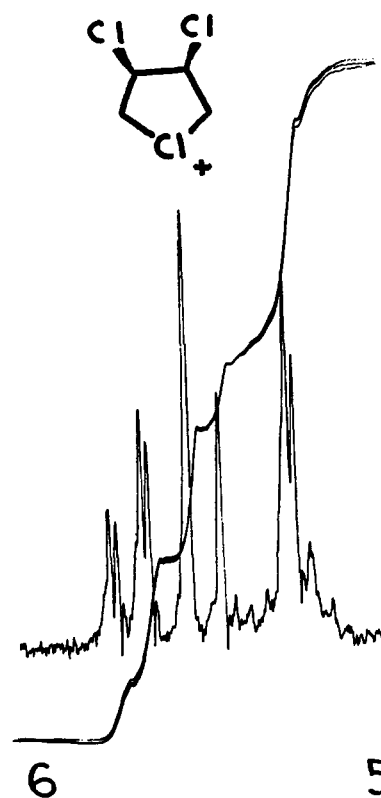
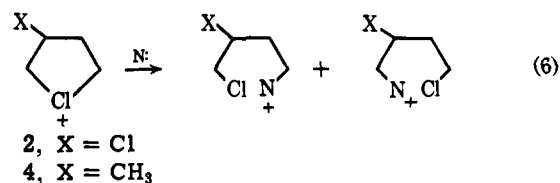















Figure 3. Nmr spectrum (SO_2 , -60° , external TMS capillary): the *cis*-3,4-dichlorotetramethylenchloronium ion **9**.



N: = CH_3OH , $(\text{CH}_3)_2\text{O}$, $\text{CH}_3\text{CO}_2\text{H}$, $\text{CF}_3\text{CO}_2\text{H}$














fluoroacetic acid, according to the general equation 6. The products from these reactions and their relative percentages are given in Tables II and III for ions **2** and

Table II. Direction of Opening of 3-Chlorotetramethylenechloronium Ion

Ion	Nucleophile	Product	Relative %	Product	Relative %
	CH ₃ OH		5.5 ^a		94.5
			5.4 ^b		94.6
			4.3 ^c		95.7
	CH ₃ OCH ₃		4.9 ^a		95.1
			4.4 ^b		95.6
			3.5 ^c		96.5
	CH ₃ CO ₂ H		2.7 ^d		97.3
					
	CF ₃ CO ₂ H		1.5 ^d		98.5

^a Ion solution added to nucleophile. ^b Nucleophile added to ion solution. ^c Ion solution added to nucleophile in SO₂. ^d Nucleophile in SO₂ solution added to ion.

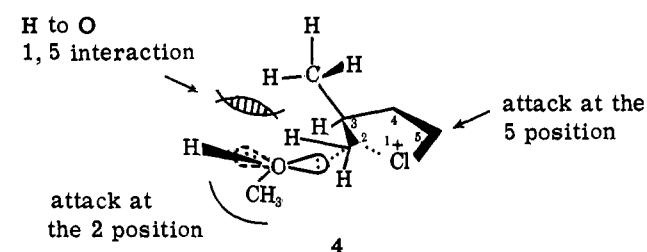
Table III. Direction of Opening of 3-Methyltetramethylenechloronium Ion

Ion	Nucleophile	Product	Relative %	Product	Relative %
	CH ₃ OH		22.6 ^a		77.4
			26.4 ^b		73.6
			21.4 ^c		78.6
	CH ₃ OCH ₃		16.5 ^c		83.5
	CH ₃ CO ₂ H		22.0 ^d		78.0
					
	CF ₃ CO ₂ H		22.0 ^d		78.0

^a Ion solution added to nucleophile. ^b Ion solution added to nucleophile with added K₂CO₃. ^c Nucleophile added to ion solution. ^d Nucleophile in SO₂ added to ion solution.

4, respectively. It will be noted that the ultimate product obtained when dimethyl ether is the nucleophile is the same ether obtained with the nucleophile methanol.

The data in Table III for the methylated ion, 4, can be interpreted as reflecting the probability that the nucleophile, in order to give attack at the 2 position (Chart I), approaches with interfering groups oriented

Chart I

away from the substituent CH₃ group. A small 1,5 interaction (overlapping circles) presumably hinders

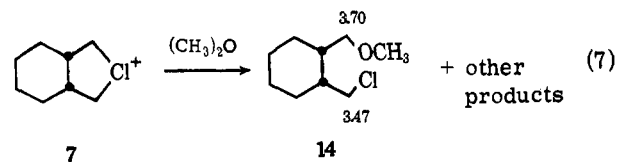
attack at C-2. Attack at the 5 position is relatively unhindered. Accordingly, it is not surprising that the major isomer obtained from reaction of nucleophiles with the methylated chloronium ion 4 is that arising from attack at this position.

Similar steric considerations may be involved for attack at the 2 position of the 3-chloro-substituted chloronium ion 2. However, the 3-chloro substituent also may lead to a decreased rate of attack at the 2 position owing to the inductive influence of the substituent. This possibility is suggested by the sixfold rate depression for the trifluoroacetolysis of 3-chloro-1-butyl *p*-nitrobenzenesulfonate (nosylate) relative to the rate for ethyl nosylate.¹⁰ However, the results (Table II) also may reflect an increase in the rate of attack at the 5 position, owing to the inductive effect of the 3-chloro substituent, which may selectively increase the leaving group reactivity of positive chlorine at C-5. That the latter effect plays a part in the control of orientation is supported by rate enhancements in the reactions of 2 with acetic and trifluoroacetic acid⁶ compared to the corresponding reactions of the unsubstituted tetramethylenechloronium ion.

Inductive effects in solvolyses are solvent dependent as shown by the solvolysis rate data for 4-chloro-2-butyl tosylate relative to that for 2-butyl tosylate in acetic ($k_H/k_X = 18.7$), formic ($k_H/k_X = 129$), and trifluoroacetic ($k_H/k_X = 329$) acid.¹¹ The increased selectivity for opening of the chlorinated ion away from the substituent when the reactant is CF₃CO₂H presumably reflects the enhanced inductive effect characteristic of a weakly nucleophilic reactant. It may be envisioned that the CF₃ group forces the transition state charge away from the carbonyl carbon and toward the oxygen atom which is closer to the inductive substituent. Significantly, the methylated ion 4, having only a sterically interacting substituent, does not show the effect.

As described earlier, the attempted preparation of ion 4 actually gave a mixture of 4 and 5. The relative percentages of the products from the reaction of this ion solution with methanol both before and after rearrangement are given in Table IV. Only very small amounts of the *sec*- and *tert*-methyl ethers 12 and 13 were formed when the nucleophile was dimethyl ether. Presumably the intermediate oxonium ions in these instances react by elimination or other unknown pathways.

Reaction of ion 7 with dimethyl ether followed by preparative gas chromatography gave the major product whose nmr spectrum (in trifluoroacetic acid) is shown in Figure 4. It was interpreted as that of *cis*-1-chloro-2-methoxymethylcyclohexane (14) (eq 7).



The doublets at δ 3.47 and 3.70 are assigned to the methylene groups next to chlorine and methoxyl, respectively, and the singlet at δ 3.53 to the methoxyl group. It was possible by decoupling experiments to

(10) P. E. Peterson and J. F. Coffey, *J. Amer. Chem. Soc.*, **93**, 5208 (1971).

(11) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967).

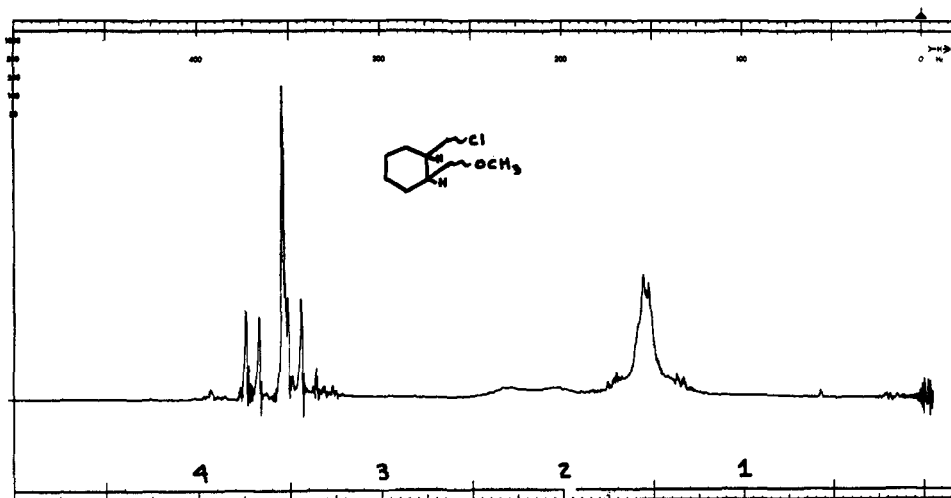
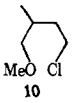
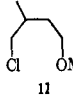
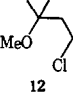
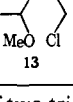


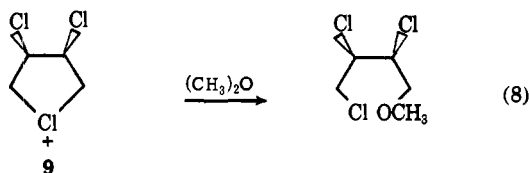
Figure 4. Nmr spectrum (trifluoroacetic acid): product from the reaction of the bicyclic tetramethylenchloronium ion 7 with dimethyl ether, *cis*-1-chloromethyl-2-methoxymethylcyclohexane (14).

Table IV. Relative Percentages of Products Obtained from Reaction of Methanol with Unwarmed and Warmed Solutions of 1,4-Dichloro-2-methylbutane in $\text{SbF}_5\text{-SO}_2$

Product	Relative % of product Unwarmed solutions ^a	Warmed solutions
	19	
	70	
	11	55
		45

^a Average of two trials which agreed within 2%.

collapse each doublet of the spectrum in Figure 4 individually into a singlet, confirming the coupling pattern. Nmr analysis indicated that reaction of the dichlorochloronium ion 9 with dimethyl ether gave the expected ether shown in eq 8.



Thermal Stability of Ions

The thermal stability of the cyclic tetramethylenchloronium ion appears to be increased by the addition of 3,4-dichloro substituents. Warming ion 9 for 6 min at 0° had no effect on the nmr spectrum of the ion. However, warming to 30° caused complete disappearance of all spectral peaks characteristic of the ion

species. This stability can be contrasted with that of ion 2 and the unsubstituted tetramethylenchloronium ion which show a decrease in intensity of nmr spectral peaks at -20°.³

Experimental Section

Nmr spectra of starting materials, ions, and reaction products were obtained on a Varian HA-100D spectrometer equipped with a variable temperature probe and a Varian 1024 time averaging computer. A Hewlett-Packard Model 521C electronic counter and Model 200AB audio oscillator made decoupling experiments possible. Distillations were done using an 18-in. spinning band column, and gas chromatography was performed using a Hewlett-Packard Model 5750 flame ionization gas chromatograph equipped with 1/8-in. 6-ft stainless steel columns.

1,2,4-Trichlorobutane was prepared from 4-chloro-1-butene (Columbia) by the procedure of Poutsma for the chlorination of norbornene under ionic conditions.¹² Distillation afforded 1,2,4-trichlorobutane: bp 80.0–80.5° (20 mm) (lit.¹³ for material prepared by a less advantageous procedure 79–83° (12 mm)); nmr (CCl_4) δ 4.25 (m, 1, CHCl), 3.72 (m, 4, CH_2Cl), 2.0–2.6 (m, 2, CH_2).

4-Chloro-1,2-epoxybutane. Sodium acetate (4.7 g, 0.057 mol) in 38.1 g (0.20 mol) of 40% peracetic acid was added over 20 min to 4-chloro-1-butene (14.4 g, 0.16 mol) in 75 ml of methylene chloride, keeping the temperature between 20 and 30°. The reaction was stirred at room temperature (28°) for 20.5 hr. Sodium hydroxide (75 ml of 40%) was added slowly to the reaction mixture followed by 70 ml of water. The methylene chloride layer was extracted and dried over a molecular sieve. Distillation gave 8.0 g (47%) of 4-chloro-1,2-epoxybutane: bp 62° (40 mm); nmr (CCl_4) δ 3.60 (t, 2, CH_2Cl), 2.96 (m, 1, CH_2CH), 2.69 (m, 1) and 2.43 (m, 1) ($\text{CH}_2\text{-O}$)CH, and 1.93 (m, 2, CH_2).

4-Chloro-1-methoxy-2-butanol. To a flask was added 25 ml (25 g, 0.62 mol) of methanol and 0.166 g (0.0072 mol) of sodium. 4-Chloro-1,2-epoxybutane (7.96 g, 0.075 mol) was added dropwise and the reaction mixture refluxed for 2.5 hr. Distillation gave 5.93 g (58%) of 4-chloro-1-methoxy-2-butanol: bp 65° (3.3 mm); nmr (CCl_4) δ 3.35 (s, 3, OCH_3). Our data do not exclude the possible presence of small amounts of isomer derived from the opposite mode of epoxide ring opening, although the spectra do not suggest the presence of a second isomer.

2,4-Dichlorobutyl Methyl Ether. To a flask 4.20 g (0.03 mol) of 4-chloro-1-methoxy-2-butanol and three drops of pyridine were added. Thionyl chloride (3.57 g, 0.03 mol) was then added dropwise after which the reaction mixture was heated for 3.5 hr at 80°. Distillation gave 2.24 g (48%) of 2,4-dichlorobutyl methyl ether:

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(13) A. Rieche, H. Gross, and E. Hoefl, *J. Prakt. Chem.*, 28, 178 (1965).

bp 49° (6 mm); nmr (CCl₄) δ 4.12 (m, 1, CHCl), 3.4–3.8 (m, 4, CH₂Cl and CH₂OMe), 3.36 (s, 3, OCH₃), and 1.98–2.34 (m, 2, CH₂).

4-Methoxy-1-butene. To a flask were added 18.0 g (0.25 mol) of 3-buten-1-ol, 60 ml of diglyme, and finally 5.75 g (0.25 mol) of sodium under nitrogen. The reaction was stirred at 50–60° for 22 hr. Methyl iodide was then added slowly, and the reaction mixture was stirred for 15 min. Ether extraction followed by distillation gave 9.03 g (42%) of 4-methoxy-1-butene: bp 68–69° (760 mm) (lit.¹⁴ 68–69° (750 mm)); nmr (CCl₄) δ 5.57 (m, 1, CH=C), 5.00 (d, 2, CH₂=C), 3.31 (t, 2, CH₂OMe), 3.23 (s, 3, OCH₃), and 2.23 (q, 2, CH₂).

3,4-Dichlorobutyl Methyl Ether. Into a chlorination apparatus¹² was put 9.05 g (0.105 mol) of 4-methoxy-1-butene in 100 ml of carbon tetrachloride. Chloride (7.5 g, 4.8 ml, 0.105 mol) was condensed in a side arm and allowed to bubble through the carbon tetrachloride solution using oxygen as a carrier gas. Distillation gave 7.95 g (48%) of 3,4-dichlorobutyl methyl ether: bp 68° (35 mm) (lit.¹⁵ 120° (760 mm)); nmr (CCl₄) δ 4.20 (m, 1, CHCl), 3.63 (m, 4, CH₂Cl and CH₂OMe), 3.30 (s, 3, OCH₃), and 2.26 and 1.80 (m both, 2, CH₂). Nmr indicated the absence of 2,4-dichlorobutyl methyl ether, whose spectrum was available.

2,4-Dichloro-1-butanol. The procedure of Cristol and Eliar used for the preparation of 2-chloro-1-butanol from 1-butene was used.¹⁶ 4-Chloro-1-butene (10.0 g, 0.111 mol) was added to chromyl chloride (31.0 g, 0.20 mol) in 60 ml of carbon tetrachloride at 0°. The solid formed was filtered, washed with carbon tetrachloride, and hydrolyzed slowly with cold sodium bisulfite solution keeping the temperature below 5°. Ether extraction and evaporation of the ether gave 4.74 g (30%) of the two isomeric alcohols 2,4-dichloro-1-butanol (major product) and 1,4-dichloro-2-butanol. The alcohols could not be distilled or gas chromatographed owing to cyclization of the 2,4-dichloro-1-butanol to tetrahydrofuran type derivatives at elevated temperatures.

2,4-Dichloro-1-butyl Trifluoroacetate. To the crude 2,4-dichloro-1-butanol (4.7 g, 0.033 mol) reaction mixture in 10 ml of carbon tetrachloride, trifluoroacetic anhydride (14.0 g, 0.066 mol) was added. The carbon tetrachloride layer was removed, washed, and dried over magnesium sulfate. Distillation afforded 1.88 g (23.9%) of 2,4-dichloro-1-butyl trifluoroacetate which was shown to be approximately 90% pure by gas chromatography: bp 84–86° (6 mm); nmr (CCl₄) δ 4.54 (m, CH₂O₂CCF₃), 4.45 (m, CHCl), 4.03 (s, impurity), 3.74 (t, CH₂Cl), 3.08 (t, impurity), 2.24 (t, CH₂).

3,4-Dichloro-1-butanol. Chlorine (4.5 g, 0.063 mol) was bubbled through 3-buten-1-ol (5.0 g, 0.068 mol) in 12 ml of carbon tetrachloride by the same procedure used to prepare 1,2,4-trichlorobutane.¹² The solvent was removed on a rotary evaporator: nmr (CCl₄) δ 5.06 (s, OH), 4.45 (m, CHCl), 3.76 (m, CH₂OH), 2.26 and 1.89 (m, CH₂). 3,4-Dichloro-1-butanol, like 2,4-dichloro-1-butanol, could not be distilled because of the cyclization reaction mentioned previously.

3,4-Dichloro-1-butyl Trifluoroacetate. To half of the crude 3,4-dichloro-1-butanol (4.86 g, 0.034 mol assuming theoretical yield from the above reaction) in 10 ml of carbon tetrachloride, trifluoroacetic anhydride (14.3 g, 0.068 mol) was added. The carbon tetrachloride layer was washed with cold water and dried over magnesium sulfate. A short-path microdistillation afforded 1.21 g (15% overall yield from 3-buten-1-ol) of 3,4-dichloro-1-butyl trifluoroacetate: bp 100–105° (2.5 mm); nmr (CCl₄) δ 4.58 (m, CH₂O₂CCF₃), 4.16 (m, CHCl), 3.75 (eight-line AB portion of ABX spectrum, $J_{AB} = 11.5$, $J_{AX} = 8.0$, $J_{BX} = 4.5$ Hz, CHClCH₂Cl), 2.53 (m, 1, CH₂), 2.14 (m, 1, CH₂). Irradiation of the multiplet at δ 2.53 caused the multiplet at 4.58 to simplify to approximate a singlet demonstrating that the trifluoroacetate group is terminal and has not migrated: nmr (C₆H₆) δ 3.92 (four-line X₂ portion of ABX₂ spectrum, $J_{AX} = 7$, $J_{BX} = 5$ Hz, CH₂O₂CCF₃), 3.55 (m, CHCl), 3.07 (m, CHClCH₂Cl), 1.2–1.9 (m, CH₂).

1,4-Dichloro-2-methylbutane. Reaction of 2-methyl-1,4-butanediol (Columbia) (10.4 g, 0.10 mol) with thionyl chloride (23.8 g, 0.20 mol) and pyridine (10 drops) followed by distillation gave 6.35 g (45%) of 1,4-dichloro-2-methylbutane: bp 68° (20 mm) (lit.¹⁷

168–169° (760 mm)); nmr (CCl₄) δ 3.54 (t, 2, CH₂CH₂Cl), 3.47 (d, 2, CHCH₂Cl), 2.13 (m, 1, CHCH₃), 1.80 (m, 2, CCH₂C), and 1.06 (d, 3, CH₃); nmr (SO₂, –60°, external TMS capillary) 3.42 (t, 2, CH₂CH₂Cl), 3.32 (d, 2, CHCH₂Cl), 1.85 (m, 1, CHCH₃), 1.50 (m, 2, CCH₂C), and 0.76 (d, 3, CH₃).

Ethyl α-Methyl-γ-chlorobutyrate. Following the procedure of Ioffe and Kuznetsov,¹⁸ a stream of dry hydrogen chloride was passed for 4 hr into a boiling solution of α-methyl-γ-butyrolactone (Aldrich) (18.0 g, 0.18 mol) in 225 ml of anhydrous ethanol. The alcohol was distilled off and the residual product poured into water and extracted with ether. Drying with magnesium sulfate and removal of the ether afforded 11.2 g (43.5%) of crude ethyl α-methyl-γ-chlorobutyrate which was 90% pure by gas chromatography (lit.¹⁷ bp 80–82° (15 mm)); nmr (CCl₄) δ 4.11 (q, $J = 7$ Hz, CO₂CH₂), 3.53 (t, $J = 6.5$ Hz, CH₂Cl), 3.3–3.6 (m, small impurity peaks), 2.66 (sextet, $J = 7$ Hz, CHCH₃), 1.6–2.14 (m, CH₂), 1.25 (t, $J = 7$ Hz, CO₂CH₂CH₃), 1.18 (d, $J = 7$ Hz, CHCH₃).

4-Chloro-2-methyl-1-butanol. For the preparation of 4-chloro-2-methyl-1-butanol the procedure of Ioffe and Kuznetsov was used.¹⁸ To a solution of lithium aluminum hydride (3.80 g, 0.100 mol) in 160 ml of anhydrous ether, cooled to 0°, was added ethyl α-methyl-γ-chlorobutyrate (11.2 g, 0.067 mol) in 110 ml of ether over 1 hr. After standing 0.5 hr at 0°, ethyl acetate (3.08 g, 0.035 mol) was added and then an excess of 10% sulfuric acid. The ether layer was collected and dried with magnesium sulfate and the ether removed under vacuum. The 4-chloro-2-methyl-1-butanol was quickly distilled giving 3.45 g (42%): bp 67–70° (5 mm) (lit.¹⁸ 77–78° (6 mm)). Gas chromatography of the product, on Silicon Oil DC-550 at 130°, gave 15% of a low boiling impurity which was thought to be 2-methyltetrahydrofuran, most probably formed during distillation: nmr (CCl₄) δ 3.50 (m, CH₂OH and CH₂Cl), 1.5–2.0 (m, CH₂), 1.94 (d, $J = 6$ Hz, CHCH₃).

4-Chloro-2-methylbutyl Methyl Ether. A 0.344 *N* solution of diazomethane in ether was prepared by the method of Moore and Reed¹⁹ and standardized with benzoic acid.²⁰ The methyl ether was prepared by titrating a solution of 4-chloro-2-methyl-1-butanol (3.25 g, 0.028 mol) and fluoroboric acid (2 drops) in 7 ml of ether at 0° with the diazomethane solution by the procedure of Neemans, *et al.*,²¹ and Tao.²² Pure 4-chloro-2-methylbutyl methyl ether was obtained by preparative gas chromatography on 1/4 in. Silicon Oil DC-550 at 130°: nmr (CCl₄) δ 3.57 (t, $J = 7$ Hz, CH₂Cl), 3.28 (s, OCH₃), 3.19 (d, $J = 5$ Hz, CH₂OMe), 1.5–2.1 (m, CH₂), 0.93 (d, $J = 6$ Hz, CHCH₃). A small doublet at 1.03 probably due to the methyl group of 2-methyltetrahydrofuran was also present.

4-Chloro-2-methyl-1-butyl Acetate. Acetic anhydride (1.19 g, 0.0117 mol) was added slowly to a stirred solution of 4-chloro-2-methyl-1-butanol (0.72 g, 0.0059 mol) in 2 ml of carbon tetrachloride at 0°. The reaction mixture was washed with cold water, dried, and concentrated: nmr (CCl₄) δ 3.92 (d, $J = 6$ Hz, CH₂O₂CCH₃), 3.57 (t, $J = 6$ Hz, CH₂Cl), 2.18 (s, CH₃CO₂H), 2.01 (s, CH₃CO₂CH₂CH(CH₃)CH₂CH₂Cl), 1.5–2.2 (m, CH₂), 0.97 (d, $J = 6$ Hz, CHCH₃) and minor peaks due to the other isomer 4-chloro-3-methyl-1-butyl acetate at 4.10 (t, $J = 6$ Hz, CH₂CO₂CH₃), 3.47 (d, $J = 6$ Hz, CH₂Cl), 1.99 (s, CH₃CO₂CH₂CH₂CH(CH₃)CH₂Cl), 1.05 (d, $J = 6$ Hz, CHCH₃).

1,2,4-Tribromobutane. A flask containing 10.0 g (0.074 mol) of 4-bromo-1-butene in 10 ml of carbon tetrachloride was stirred while bromine (12.3 g, 0.77 mol) was added. Distillation gave bp 72° (0.5 mm) (lit.²³ 112–113° (13 mm)); nmr (CCl₄) δ 4.35 (m, 1, CHBr), 3.60 (m, 4, CH₂Br), and 2.50 (m, 2, CH₂).

cis-1,2-Bis(hydroxymethyl)cyclohexane. Using a procedure similar to that of Nystrom, *et al.*,²⁴ hexahydrophthalic anhydride (46.2 g, 0.30 mol) in 700 ml of anhydrous ether was added to 19.0 g (0.50 mol) of lithium aluminum hydride in 600 ml of anhydrous ether with stirring. Excess lithium aluminum hydride was allowed to react with water. Evaporation of the ether gave 35.8 g of crude cis-1,2-bis(hydroxymethyl)cyclohexane.

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cis-1,2-Bis(chloromethyl)cyclohexane. Reaction of crude *cis*-1,2-bis(hydroxymethyl)cyclohexane (35.8 g, 0.25 mol) containing 30 drops of pyridine with thionyl chloride (59.5 g, 0.50 mol) followed by distillation afforded 19.5 g (43.3%) of *cis*-1,2-bis(chloromethyl)cyclohexane: bp 134° (20 mm); nmr (CCl₄) δ 3.45 (d, 4, CH₂Cl), 2.15 (m, 2, methine hydrogen), and 1.54 (m, 8, methylene ring hydrogens); nmr (SO₂, -60°, external TMS capillary) δ 3.30, 1.87, and 1.21, respectively.

meso-1,2,3,4-Tetrachlorobutane. A flask containing 31.3 g (0.25 mol) of 1,4-dichloro-2-butene (Columbia) in 100 ml of carbon tetrachloride was cooled in a Dry Ice-acetone bath while chlorine (17.4 g, 11.1 ml, 0.25 mol) was carried into it by a stream of oxygen¹² under subdued light. The reaction mixture was allowed to warm, and then was distilled.²⁵ Heating tape was wrapped around the head of the spinning band column to keep the *meso*-1,2,3,4-tetrachlorobutane from solidifying. Following early liquid fractions presumably containing racemic compound, 38.4 g (78.4%) of solid *meso*-1,2,3,4-tetrachlorobutane was obtained: bp 101° (20 mm) (lit.²⁵ 130-134° (40 mm); mp 72°); nmr (CCl₄) δ 4.41 (m, 2, CHClCHCl) and 4.03 (m, 4, CH₂Cl).

Preparation of Ions. The halonium ions were prepared by weighing the antimony pentafluoride into a small volumetric or erlenmeyer flask and dissolving it in 10 ml of SO₂ at -65°. A calculated amount of dihalide was then added *via* a syringe to make the molar ratio SbF₅:dihalide 4:1. Concentrations of the various halonium ions ranged from 0.2 to 0.8 M. Ion solutions were transferred to nmr tubes with a low-temperature transfer pipet.

All chemical shifts in SO₂ are reported relative to external TMS capillaries which sometimes contained 5-10% acetone, an internal area standard which has been mentioned. Chemical shifts (-60°) for all halonium ions prepared are given in Table I.

Reactions of Ions with Nucleophiles. The ions, in each case, were treated with excess nucleophile and allowed to warm to room temperature. After most of the SO₂ had evaporated carbon tetrachloride was added and the solution was washed with water. The CCl₄ solution was dried with either magnesium sulfate or 5A molecular sieve. Four methods of combining the reactants were shown to have an insignificant effect on the results as indicated by the data in Tables II and III.

Relative amounts of isomeric products from the reaction of ions 2 and 4 with nucleophiles were determined in most cases by synthesizing either both isomers or only the minor isomer for identifi-

cation of nmr peaks in the product spectrum. Integration of expanded nmr spectra, described below, gave the relative amounts of the isomers. In the case of methyl ethers derived from 3-chlorotetramethylenchloronium ion 2, the methoxyl peaks at δ 3.30 and 3.36 in 3,4-dichlorobutyl methyl ether and 2,4-dichlorobutyl methyl ether, respectively, were used for quantitative determinations.

Acetates derived from 2 were analyzed by shifting the hydrogen nmr spectra with successive addition of europium(III) tris-1,1,1,2,2,2,3,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (Norell Chemical Co., Inc., Landing, N. J.) until the O₂CCH₃ singlets in 2,4-dichloro-1-butyl acetate and 3,4-dichloro-1-butyl acetate were separated from underlying interfering peaks and from each other (δ 3.29 and 3.21, respectively).

Trifluoroacetates derived from 2 were analyzed by their nmr spectra in benzene solvent. In this solvent 2,4-dichloro-1-butyl trifluoroacetate exhibits a broad singlet at δ 3.81 attributed to accidentally identical chemical shifts for the nonequivalent CH₂-O₂CCF₃ protons and the CHCl proton. The height of this peak in the unknown mixture from 2 and in the mixture to which known amounts of 2,4-dichloro-1-butyl trifluoroacetate was added was used in quantitative analysis.

The products of reaction of the 3-methyltetramethylenchloronium ion 4 with methanol or dimethyl ether were analyzed by nmr, using areas of the methyl doublets at δ 1.03 and 0.93 for 4-chloro-3-methylbutyl methyl ether and 4-chloro-2-methylbutyl methyl ether, respectively, and the area for the singlet of the tertiary ether, 4-chloro-2-methyl-2-butyl methyl ether, in cases where the latter compound was present.

The acetates derived from ion 4 were analyzed using areas of the doublet at δ 3.92 and triplet at 4.10 in 4-chloro-2-methyl-1-butyl acetate and 4-chloro-3-methyl-1-butyl acetate. Trifluoroacetates derived from 4 were analyzed similarly using the doublet at δ 4.25 and the triplet at 4.42.

Stability Studies. Stability measurements on the ions were made by first taking the spectrum of the ion at -60° with a TMS-acetone capillary and measuring the ion peak heights with respect to the acetone peak in the capillary. The nmr tube was then warmed either in the instrument or in a constant temperature bath for a measured length of time. The relative decrease of the ion peak heights was attributed to decomposition of the ion.

Acknowledgment. Support by the National Science Foundation (Grant No. GP-10919) is gratefully acknowledged.

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