

Onium Ions. X. Structural Study of Acyclic and Cyclic Halonium Ions by Carbon-13 Nuclear Magnetic Resonance Spectroscopy.¹ The Question of Intra- and Intermolecular Equilibration of Halonium Ions with Haloalkylcarbenium Ions

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Abstract: A comprehensive study of the structure of acyclic and cyclic halonium ions was carried out by cmr spectroscopy. The proton decoupled carbon-13 nmr spectra of 10 dialkylhalonium ions, 17 arylalkylhalonium ions, 14 cyclic ethylenehalonium ions, and 11 cyclic tetramethylenehalonium ions have been obtained using the Fourier transform method. The structure of the ions is discussed on the basis of the carbon-13 chemical shift data. For the cyclic halonium ions the structures considered were the symmetrically and unsymmetrically bridged ions, an equilibrium mixture of the open chain halocarbenium ions, and of bridged halonium ions with open chain β -haloalkylcarbenium ions. The α - and β -substituent effects of positively charged halogen atoms on carbon-13 chemical shifts are summarized and correlated with similar effects for halogens. Substituent effects of positively charged chlorine, bromine, and iodine are compared.

Halonium ions are important reaction intermediates in halogenation reactions. With the development of highly acidic and low-nucleophilicity solvent systems such as $\text{SbF}_5\text{-SO}_2(\text{SO}_2\text{ClF})$ solutions the preparation and direct observation, even isolation, of stable halonium ions have become possible.⁴⁻⁹ Halonium ions are now recognized as an important class of onium compounds in their own right and their chemistry is rapidly being explored.

Halonium ions can be classified into acyclic and cyclic halonium ions. Acyclic halonium ions include dialkylhalonium ions,⁴ alkylarylhalonium ions,⁵ and diarylhalonium ions.⁶ Di- and trihalonium ions^{7,10} have also been prepared and characterized by nmr spectroscopy. Cyclic halonium ions include three-membered ring ethylenehalonium ions,⁸ five-membered ring tetramethylenehalonium ions,⁹ and six-membered ring pentamethylenehalonium ions,¹⁰ reported recently. Attempted preparation of four-membered ring trimethylenehalonium ions under similar conditions was generally unsuccessful,^{11a} although a recent report has appeared on four-membered ring fluorinated halonium ions.^{11b}

(1) Part IX: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **96**, 3560 (1974).

(2) Postdoctoral Research Investigator, 1971-1973.

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(4) (a) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969); (b) *ibid.*, **92**, 718 (1970).

(5) G. A. Olah and E. G. Melby, *J. Amer. Chem. Soc.*, **94**, 6220 (1972).

(6) (a) A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957); (b) I. Masson and E. Race, *J. Chem. Soc.*, 1718 (1937).

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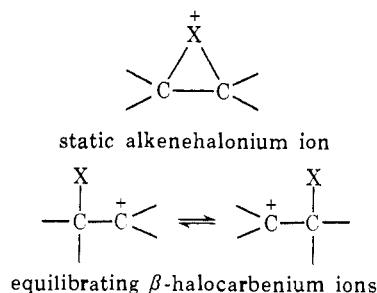
(8) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); (b) *ibid.*, **90**, 947 (1968); (c) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968).

(9) (a) G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968); (b) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968).

(10) P. E. Peterson, B. R. Bonazza, and P. M. Henrichs, *J. Amer. Chem. Soc.*, **95**, 2222 (1973).

(11) (a) G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, **94**, 1164 (1972); (b) J. H. Exner, L. D. Kershner, and T. E. Evans, *J. Chem. Soc., Chem. Commun.*, 361 (1973).

The structure of halonium ions was based so far primarily on their proton magnetic resonance spectra and other physical measurements, such as Raman spectroscopy and determination of heats of formation. Carbon-13 nuclear magnetic resonance spectroscopy is a powerful tool for studying the structure of organic ions. Some cmr spectral data of dimethylhalonium ions,^{4b} ethylenebromonium ions,^{12,13} and tetra- and pentamethylenehalonium ions¹⁰ have been reported, but



no detailed cmr study of halonium ions was yet carried out.

We now wish to report a comprehensive carbon-13 nmr spectral study of halonium ions (both acyclic and cyclic), and the evaluation of these data with regard to the structural aspects of halonium ions. In particular, for cyclic halonium ions we wanted to evaluate if the data from a sufficient number of analogs would enable a distinction to be made between possible rapidly equilibrating open chain halocarbenium ions and static bridged ions, or equilibration between the two.

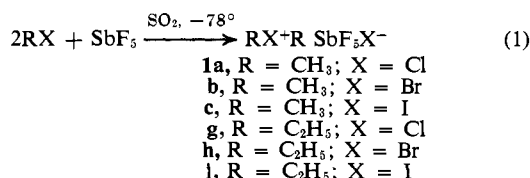
Results and Discussion

(A) Open Chain Halonium Ions. Dialkylhalonium Ions. Symmetrical dialkylhalonium ions were prepared from alkyl halides with antimony pentafluoride in SO_2 at -78° .^{4a} (For simplicity we denote the counter-

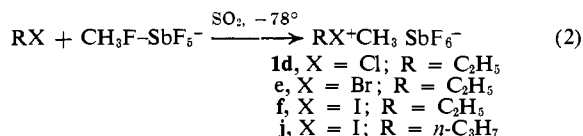
(12) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(13) G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 6877 (1971).

ion as only monomeric SbX_6^- , although its more complex nature involving dimeric (trimeric) forms, such as $\text{Sb}_2\text{X}_{11}^-$, was discussed.^{4,10)}



Unsymmetrical methylalkylhalonium ions were prepared by the methylation of the corresponding alkyl halides with methyl fluoroantimonate¹⁴ in SO₂ solution.



The ¹³C chemical shifts of dialkylhalonium ions **1a-j**, obtained by the Fourier transform method, are summarized in Table I. The assignments were made by the

Table I. Carbon-13 Chemical Shifts of Dialkylhalonium Ions^a $\text{RX}^+\text{R}'\text{SbF}_5\text{X}^-$

Ion	R	R'	X	R'			R	
				C _α	C _β	C _γ	C _α	C _β
1a	CH ₃	CH ₃	Cl	144.9			144.9	
1b	CH ₃	CH ₃	Br	156.2			156.2	
1c	CH ₃	CH ₃	I	184.3			184.3	
1d	CH ₃	C ₂ H ₅	Cl	120.3	176.9		145.8	
1e	CH ₃	C ₂ H ₅	Br	126.9	177.1		157.7	
1f	CH ₃	C ₂ H ₅	I	155.9	176.5		185.8	
1g	C ₂ H ₅	C ₂ H ₅	Cl	120.7	173.3		120.7	173.3
1h	C ₂ H ₅	C ₂ H ₅	Br	129.4	175.7		129.4	175.7
1i	C ₂ H ₅	C ₂ H ₅	I	156.9	175.1		156.9	175.1
1j	CH ₃	<i>n</i> -C ₃ H ₇	I	144.9	167.5	176.7	184.3	

^a In ppm from ¹³CS₂ in SO₂ at -30 to -40°. Whereas in recent work we also adapted referencing from Si(¹³CH₃)₄, in order to be consistent with previously published data on halonium ions, cmr shifts in this paper are still given from ¹³CS₂ reference. The conversion factor to TMS is 193.8 (capillary) and 192.8 ppm (internal).

usual procedures of Grant and coworkers.¹⁵ These include the use of "off-resonance" proton decoupling, as well as considerations of relative signal intensities and molecular symmetry. Also the observation that polar groups exert a large inductive effect on the shifts of directly attached carbons was taken into consideration.

A comparison of the carbon shifts in dialkylhalonium ions and alkanes (Table II) shows the effect of the RX⁺-group on carbon shieldings along a hydrocarbon chain. It can be seen from the available data that RX⁺- has an appreciable deshielding effect at the α and β carbons. The α effect correlates with the electronegativities of the halogens in that chlorine shows the largest deshielding effect. The β effects are nearly the same for all halogens with the least electronegative atom, iodine, as in the case of the alkyl halides,^{16c} exhibiting the largest effect.

Differences in the α-substituent effects between alkyl

(14) (a) G. A. Olah, J. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 2112 (1969); (b) G. A. Olah, J. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

(15) (a) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964); (b) D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967).

(16) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972: (a) Table 3.1; (b) Table 5.4; (c) Table 5.5; (d) Table 5.58; (e) p 201; (f) p 202; (g) p 55.

Table II. Substituent Effects of RX⁺ Groups in Dialkylhalonium Ions^a Compared with Parent Alkanes

Carbon position	Ppm ^b for ions identified in parentheses (cf. Table I)			
	X = Cl	Br	I	
	R = Methyl			
α {	CH ₃ ^c	50.9 (1a)	39.6 (1b)	11.5 (1c)
	CH ₂ ^d	67.5 (1d)	60.9 (1e)	31.9 (1f)
		10.9 (1d)	10.7 (1e)	11.3 (1f)
	R = Ethyl			
α {	CH ₃ ^c	50.0 (1d)	38.1 (1e)	10.0 (1f)
	CH ₂ ^d	67.1 (1g)	58.4 (1h)	30.9 (1i)
β	11.5 (1g)	12.1 (1h)	12.7 (1i)	

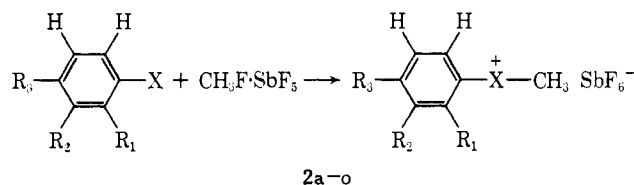
^a The differences were calculated by subtracting the chemical shifts in a dialkylhalonium ion from the shifts in the corresponding unsubstituted hydrocarbon [δ_{CH_4} , 195.8 and $\delta_{\text{C}_2\text{H}_6}$, 187.8 (ref 16a)].

^b Positive sign indicates deshielding. ^c Chemical shift difference between CH₃ and CH₃R where R = CH₃X⁺ or CH₃CH₂X⁺. ^d Chemical shift difference between CH₃CH₃ and CH₃CH₂R where R = CH₃X⁺ or CH₃CH₂X⁺.

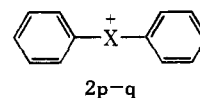
halides^{16c} and dialkylhalonium ions are shown in Table III. α-Substituent effects have been found to roughly correlate with substituent electronegativity and the larger deshielding for RX⁺ is consistent with its greater electronegativity compared with X⁻.

The available data in Table III show that the β-carbon shift in dialkylhalonium ions is shielded from the corresponding carbon in the parent alkyl halides. A similar result was observed for the carbon shieldings of protonated and parent carboxylic acid esters.¹⁷

Alkylarylhalonium Ions. Alkylaryl bromonium and alkylaryliodonium ions were recently prepared by alkylating aryl bromides or iodides with alkyl fluoroantimonates in SO₂ solution.^{5,7} Alkylarylchloronium ions have not yet been observed. In order to study the distribution of the positive charge in these ions and in particular delocalization into the aromatic ring, we have obtained the cmr spectra of a series of substituted alkylarylhalonium ions **2a-o**. The chemical shift data are summarized in Table IV.



Diarylhalonium ions have been known for many years.⁶ With the exception of diaryliodonium ions they are prepared only in very low yields by the reaction of aryldiazonium salts with the appropriate halobenzene. For comparison with alkylarylhalonium ions we have obtained the cmr spectra of two parent diphenylhalonium ions **2p** and **q**, and the results are included in Table II.



The assignment of the cmr resonances of ions **2a-q** was made by the usual procedures. In some cases assignments were made by comparison of the carbon

(17) G. A. Olah and P. W. Westerman, *J. Org. Chem.*, **38**, 1986 (1973).

Table III. Differences in Substituent Effects between Haloalkanes^a and Dialkylhalonium Ions^b

Carbon position	Ppm ^c for ions and haloalkanes identified in parentheses		
	X = Cl	Br	I
	R = Methyl		
α $\begin{cases} \text{CH}_3 \\ \text{CH}_2 \end{cases}$	23.7 (1a ; CH ₃ Cl) 33.5 (1d ; EtCl)	27.3 (1b ; CH ₃ Br) 38.5 (1e ; EtBr)	29.9 (1c ; CH ₃ I) 36.6 (1f ; EtI)
β	-1.9 (1d ; EtCl)	3.7 (1e ; EtBr)	-3.4 (1f ; EtI)
γ			0.5 (1j ; PrI)
	R = Ethyl		
α $\begin{cases} \text{CH}_3 \\ \text{CH}_2 \end{cases}$	22.8 (1d ; CH ₃ Cl) 33.1 (1g ; EtCl)	25.8 (1e ; CH ₃ Br) 36.0 (1h ; EtBr)	28.4 (1f ; CH ₃ I) 37.6 (1i ; EtI)
β	-1.3 (1g ; EtCl)	-2.3 (1h ; EtBr)	-3.0 (1i ; EtI)

^a Reference 16b. ^b Table II. ^c Positive sign indicates a deshielding in the dialkylhalonium ion.

Table IV. Carbon-13 Chemical Shifts of Alkylaryl- and Diarylhalonium Ions^a

Ion	R ₁	R ₂	R ₃	X	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	+XCH ₃	CH ₃
2a	H	H	H	Br	66.2	59.2	61.1	58.3	61.1	59.2	143.8	
2b	CH ₃	H	H	Br	64.9	51.6	58.8 ^d	56.4 ^d	60.5 ^d	57.0 ^d	144.6	170.4
2c	H	CH ₃	H	Br	64.8	58.2	46.1	56.0	59.7	63.0	143.3	170.3
2d	H	H	CH ₃	Br	68.4	57.2	60.1	45.0	60.1	57.2	143.1	170.4
2e	F	H	H	Br	81.8	28.9	73.2	55.1	59.4	64.2	143.0	
2f	H	F	H	Br	(22) ^b	(254)	(19)	(7)				
2g	H	H	F	Br	68.0	73.4	29.7	70.4	58.0	64.8	142.9	
2h	H	H	F	Br	(10)	(26)	(254)	(19)	(10)			
2i	H	H	F	Br	69.8	58.2	71.8	27.0	71.8	58.2	142.7	
2j	H	H	F	Br	(9)	(22)	(9)	(22)	(9)			
2k	H	H	F	Br	87.4	56.0	59.9	59.9	59.9	56.0	173.3	
2l	H	H	F	Br	81.1	49.4	59.7 ^d	53.8 ^d	62.0	57.7 ^d	174.5	166.0
2m	H	H	F	Br	87.1	55.3	48.4	58.6	59.9	57.7	173.5	170.8
2n	H	H	F	Br	91.0	55.6	58.7	47.0	58.7	55.6	173.5	170.8
2o	H	H	F	Br	101.7	27.2	74.6	55.1	64.2	54.4	173.4	
2p	H	H	F	Br	(22)	(205)	(22)	(10)				
2q	H	H	F	Br	89.2	68.3	30.0	70.7	58.0	59.2	172.7	
2r	H	H	F	Br	(10)	(26)	(250)	(19)	(10)			
2s	H	H	F	Br	94.0	52.6	71.9	27.1	71.9	52.6	172.7	
2t	H	H	F	Br	(10)	(257)	(22)	(22)	(10)			
2u	H	H	F	Br	83.1	52.3	52.3	83.1	52.3	52.3	172.9	
2v	H	H	F	Br	60.5	59.4 ^d	62.7 ^d	58.8	59.4	62.7		
2w	H	H	F	Br	82.7	62.3	65.1	64.6	65.1	62.3		

^a In parts per million from ¹³CS₂. Hexafluoroantimonate salts in SO₂ at -60°, unless otherwise indicated. ^b J_{13C-F} in Hz. ^c In SO₂ at -40°. ^d Assignment tentative and could be reversed between corresponding ring positions. ^e The chloride salt in SO₂ at -40°.

shifts for a particular ion with those of the homolog containing one less carbon atom. For example, the carbon resonance of the ring methyl group in methyltolylhalonium ions was assigned from a comparison with the spectrum of the corresponding methylphenylhalonium ions. The ring-carbon shifts in methyl-*o*-, *m*-, and *p*-tolylhalonium ions were assigned by a consideration of the chemical shifts in the parent methylphenylhalonium ions, and the methyl substituent effects observed by Lauterbur¹⁸ in methyl substituted iodobenzenes, nitrobenzenes, phenols, and toluenes.

The ring carbon resonance in methylfluorophenylhalonium ions was assigned on the basis of the observed carbon-fluorine coupling constants. Carbon-fluorine coupling constants usually diminish in magnitude as the number of bonds in the coupling pathway increases.

In monosubstituted benzenes the carbon shieldings of most interest are the C₁ (ipso) carbon shielding, because it occurs over the widest range of shifts, and the C₄

(para) carbon shielding, because, apart from a few exceptions, it reflects the electron-withdrawing or electron-donating ability of the substituent. These shifts in bromo- and iodobenzene, and the methylphenylbromonium and -iodonium ions are shown in Table V.

Table V. Aryl Carbon Shieldings in Monosubstituted Benzenes (C₆H₅X)

X	δ_{C} , ppm from CS ₂			
	C-1	Ortho	Meta	Para
Br ^a	70.4	61.7	62.8	66.0
+BrCH ₃ ^b	66.2	59.2	61.1	58.3
Δ	4.2	2.5	1.7	7.7
I ^a	97.0	54.8	62.1	64.0
+ICH ₃ ^b	87.4	56.0	59.9	59.9
Δ	9.6	-1.2	2.2	4.1

^a Reference 16d. ^b Table IV.

The data show that on methylation of the ring halogen, the largest downfield shifts occur for the ipso and para carbons. These changes are too large to be solvent

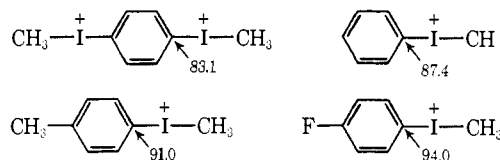
(18) (a) P. C. Lauterbur, *J. Amer. Chem. Soc.*, 83, 1846 (1961); (b) *J. Chem. Phys.*, 38, 1406, 1415, 1432 (1963).

effects alone, and suggest that the CH_3X^+ group is somewhat electron withdrawing compared with X. The smaller change in the para carbon shift for iodine reflects the lesser ability of its lone-pair electrons, compared with those of bromine, to interact with the $p\pi$ electrons of the benzene ring. The para carbon shift change in both cases is smaller than that observed (10–15 ppm) on protonation of a large number of monosubstituted benzenes (e.g., benzoic acid, benzaldehyde, nitrobenzene, etc.)¹⁹ and, compared with the π systems of the substituents in these compounds, shows the lesser ability of the halogen lone pairs to interact with the π electrons of the benzene ring.

Comparison of the relevant values in Table IV and ref 16b shows that the α -substituent effects in alkyl and aryl halides are significantly different. This is true for many other substituents apart from the halogens and most likely is attributable to the greater polarizability of the phenyl ring system. A similar difference, only larger, is observed for the α -carbon shifts of aryl- and alkylmethylhalonium ions ($\delta_{\text{C}_{\text{ipso}}}$ and δ_{CH_3}). The larger difference results from a much larger deshielding of the methyl resonance on methylation of methyl iodide (29.9 ppm for I and 27.3 ppm for Br), than in the ipso carbon resonance on methylation of aryl halide (6 ppm for iodine and 4.2 ppm for bromine).

The β -substituent effect is approximately the same for alkyl and aryl iodides (10–11 ppm) and is unaffected by methylation of the iodine atom. The situation is slightly different in bromobenzene where this effect is 5.8 ppm, or about half that in alkyl bromides.^{16c} Placing a positive charge on the bromine by methylating it is slightly deshielding from aryl bromides and slightly shielding in the case of alkyl bromides.

The effect of individual substituents in many disubstituted benzenes appears to be additive, provided that substituents are meta or para to each other.^{16e} This is shown by the ipso carbon shieldings of the $p\text{-CH}_3\text{I}^+$, $p\text{-CH}_3$ -, and $p\text{-fluoromethylphenyliodonium}$ ions, which increase to higher field in that order, in agreement with the observed para substituent effects of CH_3I^+ , methyl, and fluorine (+5.1 ppm (Table IV), -3.4 ppm,^{16d} and -4.4 ppm,^{16d} respectively). The same trend is found



in the para-substituted methylphenylbromonium ions in Table IV. Consistent with the much smaller meta substituent effects found in monosubstituted benzenes, the ipso carbon shieldings in meta-substituted methylphenylhalonium ions are almost constant. Similar trends to those above have been observed in meta and para $-\text{CH}_3$, $-\text{F}$, and $-\text{C}=\text{O}$ substituted benzoyl cations.²⁰

It has been noted^{16f} that the methyl carbon shieldings in substituted toluenes are essentially independent of the nature of the meta and para substituents, but that ortho substituents produce upfield shifts, except in the case of iodine. Our data for the CH_3I^+ and CH_3Br^+ substituents are consistent with these observations, since in

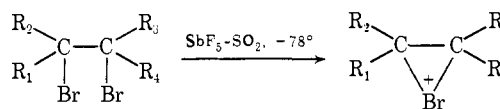
(19) G. A. Olah and P. W. Westerman, unpublished results.

(20) G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3706 (1973).

the meta and para derivatives of toluene, δ_{CH_3} is 170.6 ± 0.3 ppm (δ_{CH_3} (toluene) = 172.6) and δ_{CH_3} in the ortho CH_3I^+ derivative of toluene is 166.0 ppm. The methyl resonance in the corresponding *o*-bromo compound, unlike iodine, is essentially unchanged from that in the meta and para derivatives.

The shielding of a methyl group bonded directly to halogen in arylalkylhalonium ions is unaffected by meta or para ring substituents but is shielded slightly by an ortho ring substituent. It is of interest that these methyl group shifts in methylarylhalonium ions are deshielded by 11–13 ppm from the corresponding signals in alkylmethylhalonium ions, implying that ArX^+ is more electronegative than CH_3X^+ , since this difference is too large to be accounted for by anisotropy contributions from the phenyl ring. Perhaps this may be regarded as additional evidence for charge delocalization into the phenyl ring, except that the deshielding is of the same magnitude for both iodine and bromine.

(B) Cyclic Halonium Ions. Ethylenehalonium Ions. The ethylenebromonium ions **3a–g** were prepared as re-



3a, $R_1 = R_2 = R_3 = R_4 = \text{H}$

b, $R_1 = R_2 = R_3 = \text{H}$, $R_4 = \text{CH}_3$

c, $R_1 = R_3 = \text{H}$; $R_2 = R_4 = \text{CH}_3$

d, $R_1 = R_4 = \text{H}$; $R_2 = R_3 = \text{CH}_3$

e, $R_1 = R_2 = \text{H}$; $R_3 = R_4 = \text{CH}_3$

f, $R_1 = \text{H}$; $R_2 = R_3 = R_4 = \text{CH}_3$

g, $R_1 = R_2 = R_3 = R_4 = \text{CH}_3$

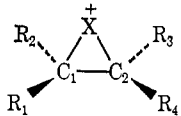
ported, from their corresponding alkyl dihalides and $\text{SbF}_5\text{-SO}_2$ solution.⁸

The *trans*- and *cis*-1,2-dimethylethylenebromonium ions²¹ (**3c** and **d**, respectively) were obtained as a mixture from either *meso*- or *dl*-2,3-dibromobutanes. The ratio of the two isomeric ions **3c** (70%) and **3d** (30%) was always the same regardless of the starting 2,3-dibromobutane. This observation was confirmed by the present spectral study (see subsequent discussion). 1,1-Dimethylethylenebromonium ion **3e** can be obtained by warming the isomeric *cis*- and *trans*-1,2-dimethylethylenebromonium ions **3c** and **3d** to -40° . The mechanism of this transformation is interesting and involves the breaking of a carbon-bromine bond, followed by subsequent 1,2-hydrogen and 1,2-methyl shifts to give ion **3e**. The two intermediates involved, **3x** and **3y**, were not observed under the experimental conditions.

1-Iodo-2-fluoroethane readily ionizes in antimony pentafluoride-sulfur dioxide with loss of fluoride ion to give the ethyleneiodonium ion **3j**. Ionization of *threo*-di-2-iodo-2-fluorobutane with $\text{SbF}_5\text{-SO}_2$ solution at -60° produced *trans*-1,2-dimethylethyleneiodonium ion **3k** (30%) and *cis*-1,2-dimethylethyleneiodonium ion **3l** (70%). Previous study showed that only iodonium ion **3l** was formed. 2-Fluoro-1-iodo-2-methylpropane²² readily ionized in antimony pentafluoride-sulfur dioxide

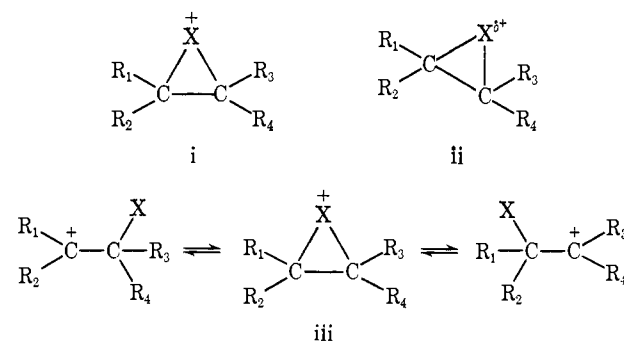
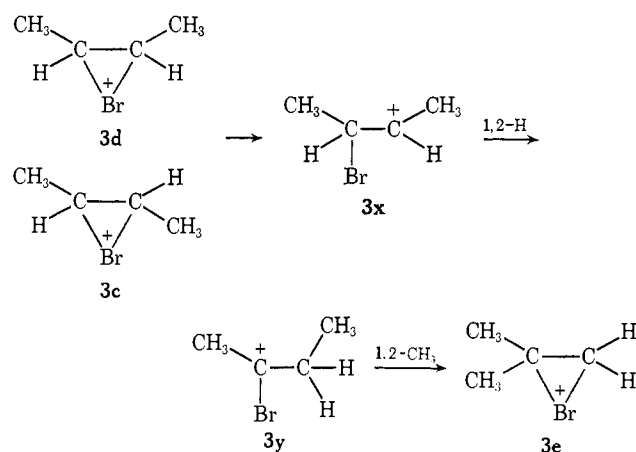
(21) In the present paper we use the polymethylene system of nomenclature for cyclic halonium ions, with carbon rather than halogen numbered one.

(22) Prepared by Dr. M. Nojima from the reaction of isobutylene with iodine in pyridine hydrogen fluoride complex (see G. A. Olah, N. Nojima, and I. Kerekes, *Synthesis*, **4**, 779 (1973)).

Table VI. Carbon-13 Chemical Shifts of Ethylenehalonium Ions^a


Ion	R ₁	R ₂	R ₃	R ₄	X	C ₁	C ₂	CH ₃ (C ₁)	CH ₃ (C ₂)
3 ^a	H	H	H	H	Br	120.8	120.8		
3b	CH ₃	H	H	H	Br	71.6	121.1	168.4	
3c ^b	CH ₃	H	CH ₃	H	Br	82.9	82.9	171.4	171.4
3d ^b	H	CH ₃	CH ₃	H	Br	85	85	176.4	176.4
3e	CH ₃	CH ₃	H	H	Br	-17.6	133.3	158.4	
3f	CH ₃	CH ₃	CH ₃	H	Br	21.0	101.1	163.3	175.6
3g	CH ₃	CH ₃	CH ₃	CH ₃	Br	54.1	54.1	167.1	167.1
3h ^c	H	H	H	H	Cl	119.7	119.7		
3i	CH ₃	CH ₃	CH ₃	CH ₃	Cl	42.1	42.1	156.8	165.8
3j	H	H	H	H	I	125.9	125.9		
3k	CH ₃	H	CH ₃	H	I	88.6	88.6	169.5	169.5
3l	H	CH ₃	CH ₃	H	I	89.8	89.8	174.6	174.6
3m	CH ₃	CH ₃	H	H	I	7.8	141.0	160.6	
3n	CH ₃	CH ₃	CH ₃	CH ₃	I	69.0	69.0	165.8	165.8

^a Parts per million from CS₂. In SO₂ at -40° unless otherwise indicated. ^b In SO₂ at -60°. ^c In SO₂ClF at -80°.



be in equilibrium with a pair of open chain β -haloalkenium ions. If one of the open ions is a primary carbenium ion it will be energetically particularly unfavorable.

Symmetrically Substituted Ethylenehalonium Ions. For the symmetrically substituted ions 3a, c, d, g, j-l, and n only structures i and iii are possible, and in the latter case there would be equal amount of the two open-ion forms.

Both chemical shift and carbon-hydrogen coupling constant data show that the structure of the ethylenebromonium ion is that of the bridged ion i. Similar considerations^{12,16} (*i.e.*, chemical shift data) applied to the other parent ethylenehalonium ions indicate that they also are symmetrically bridged ions. The ¹³C chemical shifts of the three parent ethylenehalonium ions are in the range δ_{13C} 120–126 whereas the α -carbon shifts of three related open chain dialkylhalonium ions occur over a much wider range. This most likely arises from a larger β -substituent effect in the ethylenehalonium ions because of the closer proximity of the positively charged halogen atom to the β carbon in these cyclic ions (C _{β} -C _{α} -X). The carbon shift will be dominated by charge effects, rather than by the individual differences in the nature of the halogen atoms. The large β -substituent effect in the cyclic ions explains why an approach to estimate their chemical shifts by regarding each carbon atom as subject to both an α - and β -substituent effect (Table II) is unsuccessful (except in the case of the ethylenechloronium ion where the agreement may be fortuitous).

The cmr and pmr spectra⁸ of the 1,2-dimethylethylenebromonium ion prepared from either *meso*- or *dl*-

solution with loss of fluoride ion to give the unsymmetrical iodonium ion 3m. Tetramethylethylenonium ion 3n was also prepared from 2-iodo-3-fluoro-2,3-dimethylbutane with SbF₅-SO₂ solution.

We have also recently reported the preparation and spectral characterization of the ethylenechloronium ion 3h. The last member of the parent ethylenehalonium ions to be reported was prepared from the reaction of 1-chloro-2-fluoroethane with SbF₅ in SO₂ClF.²³ Tetramethylethylenechloronium ion 3i was prepared from 2,3-dichloro-2,3-dimethylbutane with SbF₅-SO₂ solution.^{8a}

The carbon-13 chemical shifts in the 14 studied ethylenehalonium ions 3a-n are shown in Table VI.

The structures of most ions in Table VI have been discussed previously on the basis of their pmr spectral parameters⁸ and in a few cases cmr spectral parameters.^{12,13,16} In this comprehensive cmr study, now all chemical shifts were obtained and assigned by the procedures already described.

There are several structural possibilities for ethylenehalonium ions: the static symmetrically bridged ion (i) (where the C₂-X bond length is equal to the C₃-X bond length), (ii) the static unsymmetrically bridged ion (where the C₂-X bond length is not equal to the C₃-X bond length), and (iii) the halonium ion may also

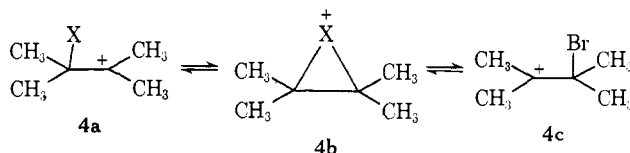
(23) G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3387 (1973).

dibromobutanes reveal the presence of cis and trans isomers. The ion is, therefore, most likely the symmetrically bridged ion since it would be extraordinary if noticeable amounts of open ion did not lead to interconversion of cis and trans isomers at a rate rapid on the nmr time scale.

The 5-ppm upfield shift in the methyl carbon shielding of the cis isomer compared with the trans isomer reflects the larger steric interactions between the methyl groups in the former case.²⁴ A similar effect of the same magnitude is observed in the two isomers of 1,2-dimethylethyleneiodonium ion.

The cis/trans ratio in the 1,2-dimethylethyleneiodonium ion depends on which precursor is used to prepare the ion. The iodonium ion, then, clearly is a symmetrically bridged ion.

The structure of the tetramethylethylenebromonium ion has been discussed in some detail.^{8,12,13,16} The cmr data first were considered inconsistent with either a bridged species **4b** or a rapidly equilibrating pair of open ions (**4a** \rightleftharpoons **4c**) so the structure of the ion was proposed to be a mixture of both forms (**4a** \rightleftharpoons **4b** \rightleftharpoons **4c**).



However, the available nmr data are still subject to two interpretations. The larger than usual substituent effect^{12,16g,25} which occurs in the C-1 and C-2 shieldings of the ethylenebromonium ion upon methyl substitution may indicate an increased carbenium ion character for the C-1 and C-2 carbons, if the ion is a static bridged ion **4b**, or some contribution of open-chain β -halocarbenium ions **4a** and **c** if the ion is a symmetrically bridged ion in equilibrium with open-ions forms. In support of the former structure, it has been argued¹³ from ¹³C chemical shift data in the tetramethylethylenephonium ion, that ion **3g** has the symmetrically bridged structure.

It is of interest that the differences in the ring carbon shifts of the three tetramethylethylenehalonium ions are larger than in the three parent ions. Iodine can accommodate positive charge better than chlorine or bromine, so more carbenium ion character at C_{1,2} exists in **3g** or **3i** than in **3n**, or there is less contribution of β -halocarbenium ions, **4a** and **c**, for iodine than for chlorine or bromine.

Unsymmetrically Substituted Ions. 1-Methyl- and 1,1-dimethylethylenebromonium ions, **3b** and **e**, may exist as unsymmetrically bridged ions (ii) or as equilibrium mixtures of the unsymmetrically bridged ion and the open chain secondary or tertiary haloalkyl cations. On the basis of cmr data for one particular temperature alone it is not possible to decide between these two possibilities.²⁶

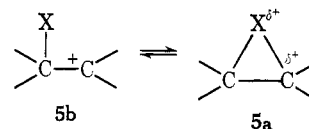
The α -substituent effect of the methyl group in ion **3b** is 49 ppm, while that of two geminal methyl groups (ion **3e**) is 138.4 ppm. Accompanying these downfield shifts at C-1 are upfield shifts of 0.3 and 12.5 ppm for the C-2 shielding in ions **3b** and **e**, respectively.

(24) T. F. Page, T. Alger, and D. M. Grant, *J. Amer. Chem. Soc.*, **87**, 5333 (1965).

(25) P. E. Peterson and B. R. Bonazzo, *J. Org. Chem.*, **38**, 1010 (1973).

(26) G. A. Olah, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3961 (1969).

The data for ions **3b** and **e** and that for β -bromocumyl ions²⁶ show β -bromine substituent effects, in ions of the type $\text{RR}'\text{C}^+\text{CH}_2\text{Br}$, of from 21 to 117 ppm. Apparently the extent to which bromine may participate in the stabilization of a positively charged β carbon may vary, depending on the electron needs of that carbon. We have recorded the cmr spectrum of ion **3e** at different temperatures to try to distinguish between a static unsymmetrically bridged ion **5a** whose cmr spectrum should be temperature independent, and an equilibrating system of a bridged ion with a β -halocarbenium ion **5b** whose cmr spectrum should vary with temperature.



The 1,1-dimethylethylenechloronium ion has already been shown to exist as a β -haloalkylcarbenium ion.^{8b} Since bromine has a greater ability than chlorine to accommodate a positive charge, we expect that the corresponding bromonium ion will be intermediate in character between a purely bridged ion and a β -haloalkylcarbenium ion, and therefore its cmr spectrum should be quite dependent on temperature.

The carbon-13 chemical shifts for the methylene and methyl carbons in ion **3e**, at several temperatures (-20 to -80°), are shown in Table VII. It was quite

Table VII. Temperature Dependence of the Carbon-13 Chemical Shifts in 1,1-Dimethylethylenebromonium Ion

Temp, °C ^b	$\delta_{13\text{C}}^a$			
	CH	CH ₂	CH ₃	Δ
-20		59.10	34.21	24.89
-30		59.27	34.19	25.08
-40	211.3	59.37	33.98	25.38
-50		59.62	34.05	25.56
-60		59.58	33.71	25.87
-70		60.09	33.76	26.34
-80	206.17	59.87	33.45	26.41

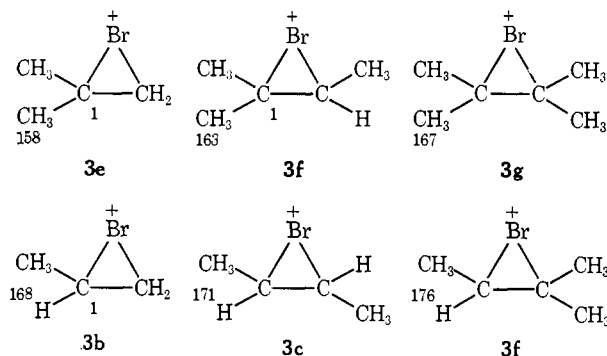
^a In SO₂; parts per million from external capillary of tetramethylsilane. ^b $\pm 1^\circ$.

impractical to obtain the C-1 shieldings for all seven temperatures in Table VII because of the very large number of FT accumulations necessary to observe this signal at the low ion concentrations obtainable for this low-temperature study. Signals were measured from external TMS and it is not known how significant are the small absolute changes for δ_{CH_3} and δ_{CH_2} shown in Table VII. However, the internal chemical shift differences ($\delta_{\text{CCH}_3} - \delta_{\text{CCH}_2}$) should be temperature independent, so that changes in its value reflect changes in the position of the equilibrium (**5a** \rightleftharpoons **5b**). An increase in the open ion form will result in a deshielding of the CH₃ and C⁺ resonances, but it is not obvious what should occur to the CH₂ absorption. In the open ion form the methylene carbon shielding will be subject to α -bromine and α -C⁺ substituent effects, while in the bridged ion it will experience a partial α -C⁺ effect and an increased bromine substituent effect since the bromine now carries more charge. (For the analogous ion in the five-membered ring series this problem does not exist because in the open ion the shielding of the

methylene carbon bonded to bromine is not subject to an α -C⁺ effect and hence should be shielded from the corresponding resonance in a bridged structure.) The observed variation in $\delta_{\text{CH}_3} - \delta_{\text{CH}_2}$ with temperature (Table VII), therefore, cannot be given a detailed explanation in terms of molecular processes, but it does signify some sort of equilibrium.

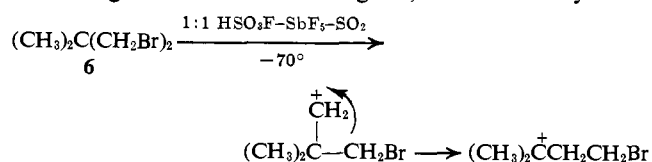
The deshielding of 5 ppm in the C-1 shielding with a 40° decrease in temperature indicates that at lower temperature there is more of the bridged ion present than at higher temperature. The relatively small change in the C-1 resonance suggests that the 1,1-dimethylethylenebromonium ion is mainly the static bridged ion in equilibrium with only a small amount of β -haloalkylcarbenium ion **5b**.

Substitution of a third methyl group into the ethylenebromonium ion results in an ion whose charge distribution is more symmetrically disposed than that in ion **3e**. This is reflected by an upfield shift of 39 ppm in the C-1 shielding compared with ion **3e**. The equivalency of the geminal methyl groups in both the pmr⁸ and cmr spectra of 1,1,2-trimethylethylene halonium ion suggests that the ion exists as an equilibrating mixture of the unsymmetrically bridged ion and an open ion form. It is, however, possible, although less likely, because of the large *cis* methyl shielding effect in ions **3c** and **d**, that both the geminal methyl carbon and proton shieldings are accidentally equivalent in the bridged ion, and that consequently equilibration does not occur.

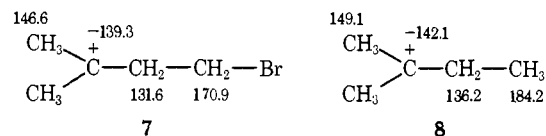


The order of the C-1 methyl shieldings in **3e-g** is the same as we would predict from a consideration of the relative degrees of electron deficiencies at C-1 and C-2 in these ions; similarly for the methyl shifts in ions **3b, c**, and **f**. For corresponding ions in both series the methyl shift is deshielded in the former case, as expected.

Attempted Preparation of Four-Membered Ring Halonium Ions. Attempts to prepare four-membered ring trimethylenehalonium ions have generally been unsuccessful.^{11a} Ionization of either dimethyl- β -bromoethylmethanol or 1,3-dibromo-3-methylbutane in $\text{HSO}_3\text{F-SbF}_5\text{-SO}_2$ solution at -78° gave an ion whose pmr spectral data showed it to be the open-chain ion **7**. We also obtained ion **7** from the ionization of 2,2-dimethyl-1,3-dibromopropane **6** with $\text{HSO}_3\text{F-SbF}_5\text{-SO}_2$ solution at -70° . The pmr spectrum of the product was identical with that obtained in the above ionizations. The following mechanism involving a 1,2-bromomethyl shift

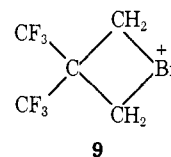


is proposed. The cmr spectrum was recorded at -70° and the chemical shifts are shown on structure **7**.



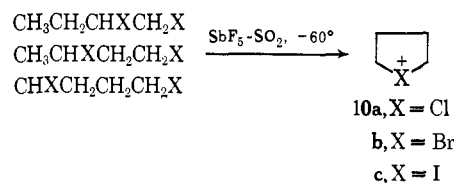
The chemical shift of the carbenium ion center ($\delta_{\text{C-1}}$ -139.3) is almost identical with the corresponding carbon shift in the dimethylethylcarbenium ion **8** ($\delta_{\text{C-1}}$ -142.1; SO_2ClF , -70°) indicating that there is no four-membered ring formation involving the bromine atom, or even significant halogen participation. This confirms the results obtained by pmr spectroscopy.

Very recently the preparation of the four-membered ring halonium ion **9** has been reported.^{11b} The relative



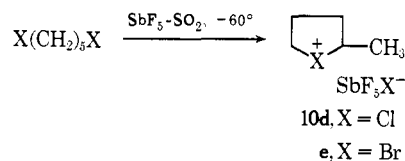
stability of ion **9**, compared with an open chain tertiary carbenium ion, formed by a similar bromomethyl shift as that above, most likely is a result of the destabilizing effect of the trifluoromethyl groups on the potential tertiary carbenium center.

Tetramethylenehalonium Ions. Ionization of either 1,2-, 1,3-, and 1,4-dihalobutanes in antimony pentafluoride-sulfur dioxide gives the parent tetramethylenehalonium ions **10a-c**.⁹ Ionization requires higher

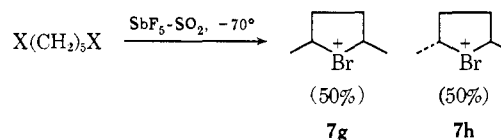


temperature (*ca.* -20°) in the case of 1,3-dihalobutanes.

1-Methyltetramethylenehalonium ions **10d** and **e**



were prepared from 1,5-dihalopentanes with $\text{SbF}_5\text{-SO}_2$ solution at -60° .^{9a} Isomeric (*cis*- and *trans*-) 1,4-dimethyltetramethylenebromonium ions (**10g** and **h**) were obtained as an equimolar mixture when 2,5-dibromohexanes were treated with $\text{SbF}_5\text{-SO}_2$ solution at -70° .⁹ The ions were also prepared by the protonation of 5-bromo-1-hexenes in superacids.⁹



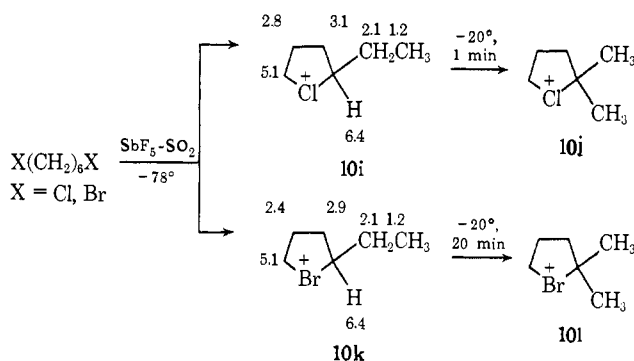
Ionization of 1,6-dihalohexanes in $\text{SbF}_5\text{-SO}_2$ solution at -78° gave 1-ethyltetramethylenehalonium ions **10i** and **k**. Proton chemical shifts in ions **10i** and **k** are

Table VIII. Carbon-13 Chemical Shifts of Tetramethylenehalonium Ions^a

10

Ion	R ₁	R ₂	R ₃	X	C ₁	C ₂	C ₃	C ₄	CH ₂	CH ₃
10a	H	H	H	Cl	115.9 (115.3) ^b	159.9 (159.2)	159.9	115.9		
10b	H	H	H	Br	123.0 (122.5)	157.4 (157.2)	157.4	123.0		
10c	H	H	H	I	142.7 (144.3)	155.0 (153.4)	155.0	142.7		
10d	CH ₃	H	H	Cl	78.2 (80.0)	150.9 (152.2)	157.1 (158.2)	117.1 (118.3)		169.9 (171.1)
10e	CH ₃	H	H	Br	86.8 (87.1)	149.0 (149.5)	156.3 (156.9)	124.0 (124.1)		169.6 (170.1)
10f	CH ₃	H	H	I	(110.2)	(146.0)	(155.4)	(144.4)		(168.9)
10g	CH ₃	H	CH ₃	Br	96.3	154.7	154.7	96.3		174.5
10h	H	CH ₃	CH ₃	Br	94.9	152.9	152.9	94.9		174.0
10j	CH ₃	CH ₃	H	Cl	-4.4	141.3	156.0	129.9		155.1
10k	CH ₃ CH ₂	H	H	Cl	76.6	151.1	156.2	124.7	161.1	177.8
10l	CH ₃	CH ₃	H	Br	42.0	143.5	156.1	128.3		159.9

^a Parts per million from ¹³CS₂. In SO₂ at -40°. ^b Values in parentheses from ref 25.



shown on the formulas. Both of these ions can be transformed into their 1,1-dimethyltetramethylenehalonium ions **10j** and **l** by warming the solutions at -20° for 1 and 20 min, respectively.

The carbon-13 chemical shift data for tetramethylenehalonium ions are shown in Table VIII. Signals were assigned by methods already discussed. The C-2 and C-3 resonances in unsymmetrically substituted tetramethylenehalonium ions were differentiated by assuming that C-1 had greater electron deficiency than C-4, and thus exerted a slightly larger deshielding α -substituent effect. The α -substituent effect of a positively charged carbon has been observed to be that of deshielding in a large number of carbenium ions.¹²

The ions in Table VIII may be divided, in the same manner as the ethylenehalonium ions, into symmetrically and unsymmetrically substituted ions.

Symmetrically Substituted Ions. Whereas the approach of applying observed α - and β -⁺XR substituent effects (Table II) to estimate the ring carbon shifts in ethylenehalonium ions was unsuccessful, good results were obtained for the five-membered ring halonium ions. For example, the methyl shift in *n*-butylalkylchloronium ion should be very similar to the methyl shift in *n*-butane (δ_{13C} 180.5),¹⁶ since the δ -substituent effect for -⁺XR should be negligible. Cyclization of the CH₃-CH₂-CH₂-CH₂-Cl⁺ group to the tetramethylenehalonium ion **10a** should result in a downfield shift of 67.5 ppm (Table II) in the methyl carbon shielding. The estimated shift of δ_{13C} 113 for C_{1,4} in ion **10a** is in good agreement with the experimentally determined value of δ_{13C} 115.9. This procedure is also successful in estimating the C_{2,3} shift of ion **10a**, as well as the C_{1,4} and C_{2,3} shifts of ions **10b** and **c**.

α - and β -Substituent effects for the RX⁺ group in the parent tetramethylenehalonium ions are therefore the same as in dialkylhalonium ions. Since the equilibrium positions of eq 1 and 2 are far to the right for primary systems, it follows that ions **10a-c** exist as static bridged species, with no rapid equilibration with open chain ω -haloalkylcarbenium ions involved.

The cmr and pmr⁹ spectra of the 1,4-dimethyltetramethylenebromonium ion reveal the presence of *cis* and *trans* isomers in equal amounts, indicating that the ion is a symmetrically bridged ion. If it is in equilibrium with an open-chain form it is a slow equilibrium with an undetectable (by nmr) amount of the open-chain ω -haloalkylcarbenium ion. The larger than usual methyl substituent effect (28 ppm) probably indicates an increased carbenium ion character for the C-1 and C-4 carbons.

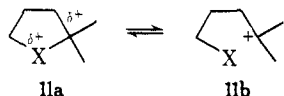
The methyl carbon absorbance of the *cis* isomer is shielded by 2.5 ppm from that in the *trans* isomer, reflecting the larger steric interaction between the methyl groups in the former case. The effect is smaller than in the *cis*- and *trans*-1,2-dimethylethylenebromonium ions indicating that the methyl groups are closer in the *cis* isomer of this ion than in *cis*-1,4-dimethyltetramethylenebromonium ion.

Unsymmetrically Substituted Ions. Replacement of a proton on C₁ by a methyl group in the tetramethylenehalonium ions results in a deshielding of 32-38 ppm in the C-1 absorbance. This may indicate an unsymmetrical bridged ion, **11a**, or be a result of these ions being in equilibrium with the open-chain ω -haloalkylcarbenium ion **11b**. However, the latter possibility is unlikely as the methyl substituent effect is approximately the same for Cl, Br, and I, so that the equilibrium constants would need to be the same in all three cases.

Furthermore, a consideration of the cmr spectrum of ion **10d** at different temperatures showed that the difference between the C-1 and C-4 chemical shifts changes only 0.7 ppm on lowering the temperature from -20 to -90°, while the corresponding change in $\delta_{C-2} - \delta_{C-3}$ is only 0.10 ppm.

Large downfield shifts at C-1 are observed on the C-1 substitution of a second methyl group into ions **10d** and **e**. In the former case the α -substituent effect is 82 ppm and in the latter 46 ppm. These large changes most likely indicate increasing carbenium ion character at C-1 with increasing methyl substitution. This is also

suggested by the comparatively large downfield methyl shifts in ions **10j** and **l** (155.1 and 159.9 ppm, respectively). The cmr spectra of ions **10j** and **l** have been recorded at different temperatures by Henrichs and Peterson,²⁷ who found that the 1,1-dimethyltetramethylenechloronium ion **10j** is in rapid equilibrium with substantial amounts of the open chain ω -chloroalkyl-carbenium ion. They also found that the 1,1,4-trimethyltetramethylenechloronium ion and 1,1-dimethyltetramethylenebromonium ion are in equilibrium with smaller amounts of the open chain ion **11b**.



In contrast to the deshielding of the C-1 shift in ions **10d-f**, **j**, and **l**, the C-4 shift becomes shielded, relative to the unsubstituted ion, with increasing methyl substitution. These effects are relatively small for ions **10d-f**, but more substantial in the 1,1-dimethyl substituted ions. For ion **10j** the shift is further shielded (14 ppm) than in the corresponding bromonium ion (5.3 ppm) because of the greater contribution of equilibrating form **11b** in the former case. This is quite reasonable considering the greater stability of a positively charged bromine atom compared with a positively charged chlorine.

Experimental Section

Preparation of Ions. The preparation of most halonium ions has been previously described. In general, they are prepared from the appropriate dihalides by the following procedure. A saturated solution of antimony pentafluoride in sulfur dioxide was prepared at -20° . Portions of this solution (2 ml) were cooled to -78° , causing some antimony pentafluoride (or its SO_2 complex) to crystallize from solution. To this suspension was added with

good stirring approximately 0.3 g of the dihalide. Slight warming was required to complete the ionization whereupon a homogeneous solution resulted. Ion concentrations were approximately 10%. Formation of the iodonium ions led to light brown solutions from which darkly colored iodonium complexes precipitated if the concentration of ion was high or the solution was stored for several hours. Solutions of bromonium ions were light red or orange, and solutions of chloronium ions were light yellow.

Preparation of Dihalide Precursors. All dihalides are known from the literature and were commercially available materials or prepared by standard methods.^{5,7-9,22}

Proton Nuclear Magnetic Resonance Spectra. Pmr spectra were obtained using Varian Associates Model A56/60A and HA 100 spectrometers equipped with variable-temperature probes. External tetramethylsilane (capillary) was used as reference.

Carbon-13 Nuclear Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL 100 equipped with a broad-band proton decoupler and variable-temperature probe. The instrument operates at 25.2 MHz for ^{13}C , and is interfaced with a Varian 620i computer (16K). The combined system was operated in the pulse-Fourier transform mode, employing the Varian Fourier transform accessory. Typically 3000–5000 pulses, each of width 20–30 μsec , needed to be accumulated in order to give a satisfactory signal-to-noise ratio for all signals of interest. Field-frequency stabilization was maintained by locking on the ^{19}F signal of an external sample of hexafluorobenzene. Chemical shifts were measured from the ^{13}C signal of 5% ^{13}C -enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube. They were converted to parts per million from $^{13}\text{CS}_2$ using the experimentally determined conversion factor; $\delta_{\text{CS}_2, \text{TMS}} 193.8$.

Some spectra were obtained using a Varian Associates Model HA-100 equipped with a Fourier transform accessory (V-4357 Pulsing and Control Unit), broad-band proton decoupler, and variable-temperature probe. The instrument, lock, and referencing systems have been described in more detail elsewhere.²⁸

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