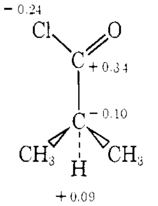
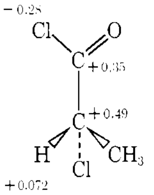
for α-chloropropionyl chloride was taken as 1.76 Å. Bond angles (deg) used were: H—C—H, 109.5; O=C—Cl, 123; C—C—CH_3, 109.5; C—C—Cl, 110.

The conformations selected of the two acid halides are shown below along with the electron densities of the atoms directly involved in the dehydrohalogenation.





It is interesting to note that the acidities of the α hydrogens of the two acid halides are relatively similar. However, the most important factor based on the CNDO/2 calculations appears to be the charge density on the α carbon. In the case of isobutyryl chloride, the α carbon possesses a partial negative charge which would be expected to poorly accommodate a negative charge buildup by formation of the enolate. However, in the case of α-chloropropionyl chloride the α carbon has a fairly high positive charge and can easily accommodate the negative charge of the enolate.

Consequently, the CNDO/2 calculations are very compatible with what has been observed experimentally and indicate it is not the acidity of the α hydrogens of the acid halides that is the mechanistic determining factor but rather the charge densities on the α carbons of the acid halides.

Experimental Section

Proton nmr spectra were recorded on a Jeolco PS-100 nmr spectrometer equipped with a variable-temperature controller employing tetramethylsilane as an internal standard and chloroform as the solvent. The infrared spectra were recorded on a Perkin-Elmer 620 infrared spectrometer equipped with a variable-temperature cell CRYO-TIP Model AC-1 by Air Products and Chemicals, Inc. Vpc was performed on an F&M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with a 10% SE-30 on acid-washed Chromosorb W (60–80 mesh).

Hexane and triethylamine were distilled from sodium and stored over Linde Type 4A molecular sieve. Chloroform was dried over phosphorus pentoxide and distilled prior to use as a solvent.

Cycloadduct from Enolate Salt. To a solution of 0.1 mol of triethylamine in 200 ml of hexane at −78° was added dropwise 0.1 mol of α-chloropropionyl chloride in 10 ml of hexane. After the addition was complete, the white salt, which precipitated during the addition, was quickly separated from the reaction solution by filtration. After filtration, the salt was washed with precooled hexane. The cold salt was suspended in 100 ml of hexane containing 0.3 mol of cyclopentadiene and stirred overnight. The mixture was filtered and the filtrate concentrated on a rotatory evaporator. Distillation afforded 6 g (40%) of the cycloadduct (7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one)[9] and some α-halovinyl ester (1,2-dichloropropenyl 2-chloropropanoate).[5]

Nmr Spectra. Equal volumes of 0.1 *M* triethylamine in chloroform and 0.1 *M* acid halide in chloroform were mixed at −78°. An aliquot of the resulting solution was placed with a hypodermic syringe in a precooled nmr tube. Spectra were recorded at −60° and various higher temperatures as the probe warmed to room temperature.

Infrared Spectra. Equal volumes of 0.05 *M* triethylamine in chloroform and 0.05 *M* acid halide in chloroform were mixed at −78° and the resulting solution was injected with a precooled syringe into the cold low temperature infrared cell. Spectra were recorded as the temperature was increased.

Kinetic Runs. α-Chloropropionyl chloride (0.1 mol) in 10 ml of chloroform was added dropwise with vigorous stirring to a solution of 0.1 mol of triethylamine in 90 ml of chloroform at −78°. After the addition was complete, the reaction mixture was allowed to warm for 30 min at which time 0.3 mol of freshly distilled cyclopentadiene was added. Aliquots were withdrawn at various times and quenched in water. The hexane layer was separated, dried, and analyzed by vpc.

Acknowledgments. The authors wish to express appreciation to Arvind D. Patel, L. P. Ting, and Professor B. R. Russell for assistance with the molecular orbital calculations. The authors also express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

Halonium Ion Rearrangements. Temperature-Dependent ^{13}C Chemical Shifts as Indicators of Equilibria between Cyclic Halonium Ions and Open Carbonium Ions[1a]

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Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received March 19, 1973*

Abstract: A marked temperature dependence of the ^{13}C chemical shifts of a number of substituted tetramethylenehalonium ions, particularly 1,1-dimethyltetramethylenechloronium ion, has been observed. The dependence has been explained in terms of shifts in an equilibrium between the halonium ions and appropriate carbonium ions. The observed chemical shifts were used to calculate equilibrium constants. Additional studies have been made of the rearrangement reactions leading to 1,1-dimethyltetramethylenechloronium ion from 1,6-dichlorohexane in SbF_5–SO_2 solution. The first observed ionization product for 1,6-dihalohexanes was 1-ethyltetramethylenehalonium ion.

Averaged ^1H and ^{13}C chemical shifts of species which interconvert rapidly on the nmr time scale have been used[2,3] in calculation of equilibrium constants. It is known from the work of Olah and coworkers[4] that in carbonium ions the cationic carbon is highly de-

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(1) (a) Support by the National Science Foundation (Grant GP 30683) is gratefully acknowledged. (b) Postdoctoral investigator.

(2) A. F. Casy, "PMR Spectroscopy in Medicinal and Biological Chemistry," Academic Press, New York, N. Y., 1971, pp 123–132.

(3) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972, p 163.

(4) See, for example, (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969); (b) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

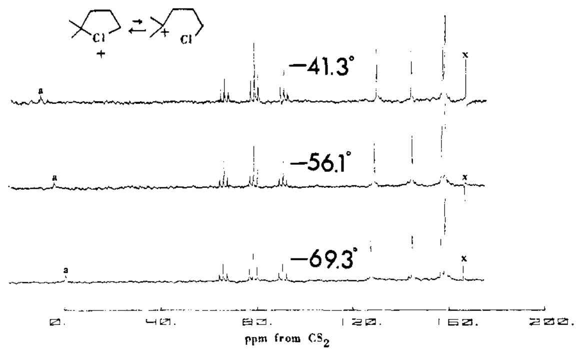
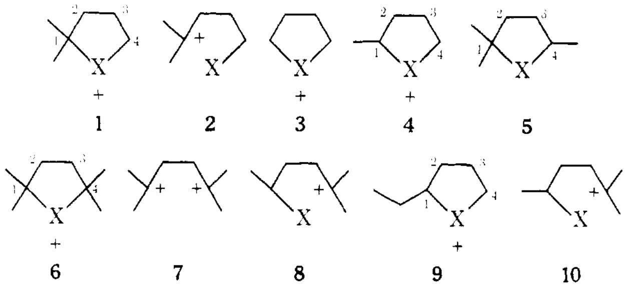


Figure 1. Temperature-dependent ^{13}C spectrum of 1,1-dimethyltetramethylenechloronium ion (**1**-Cl) with noise decoupling of protons. The peak labelled X is spurious. The triplet of triplets is due to CF_2BrCF_2Br, 78.1 ppm upfield from CS_2.

shielded. Accordingly, chemical shift differences for individual carbons of 150 ppm or more may occur when one of the species involved in an equilibrium is a carbonium ion.[4]

We now report that equilibria between tertiary carbonium ions and five-membered ring halonium ions may be demonstrated by analysis of ^{13}C chemical shifts, and, importantly, by observation of a striking temperature dependence of the chemical shifts of individual carbons. The ions which we studied resulted in part from reactions of 1,6-dihalohexanes which, in the absence of rearrangement, would have given seven-membered ring halonium ions. The previously reported rearrangement product[5] 1,1-dimethyltetramethylenechloronium ion (**1**-Cl) is shown to be formed from an intermediate 1-ethyltetramethylenehalonium ion whose properties and nmr spectra now have been obtained, along with those of the bromine and iodine analogs. The nomenclature and revised numbering (*cf.* Scheme I) of the tetramethylenehalonium ions are that adopted recently.[6]

Scheme I



Nmr Observation of Equilibrating and Nonequilibrating Ions. The ^1H nmr spectrum[7] of **1**-Cl, Scheme I, obtained by the above mentioned rearrangement,[5] was dominated by a methyl singlet, the chemical shift of which we found to be temperature dependent. The change in chemical shift (from δ 2.46 to 2.54 upon changing the temperature from −65 to −48°) suggested that the carbonium ion equilibrates rapidly on the nmr time scale with the tertiary carbonium ion **2**-Cl, whose concentration increases with increasing temperature. As expected from this hypothesis, the ^{13}C spectrum (Figure 1) shows a large temperature dependence of δ for C-1, the potential tertiary carbonium ion carbon, and a substantial temperature dependence in the opposite direction for the halosubstituted carbon. The chemical shifts for the various carbons of **1**-Cl and other ions are given in Table I and are plotted in Figure 2 *vs.* mole fractions of halonium ion in equilibrium with carbonium ion, which were calculated in a manner to be described.

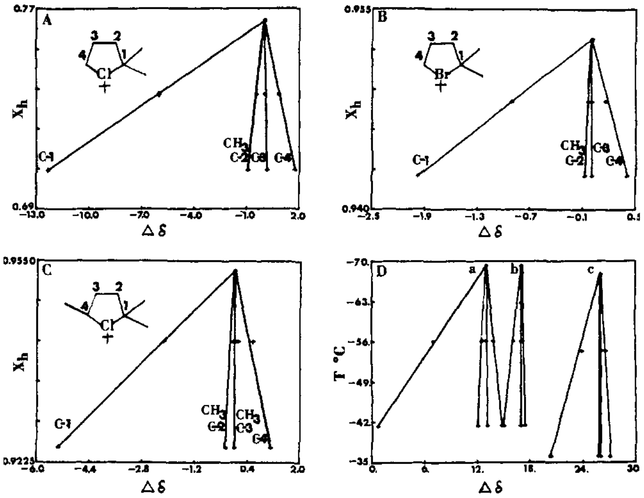


Figure 2. A, B, and C are plots of the temperature-dependent mole fraction of halonium ion (X_h) in equilibrium with carbonium ion *vs.* chemical shift differences. D is a plot of temperature *vs.* chemical shift differences for (a) 1,1-dimethyltetramethylenechloronium ion (**1**-Cl); (b) 1,1-dimethyltetramethylenebromonium ion (**1**-Br); and (c) 1,1,4-trimethyltetramethylenechloronium ion (**5**-Cl).

Table I. Temperature Dependence of ^{13}C Chemical Shifts[a]

Ion	Temp, °C	$\geqslant CX^+$		CCH_2C		CH_3
1-Cl	−69.3	1.4	127.5	144.8	156.7	158.5
	−56.1	−4.6	128.3	144.3	156.7	158.1
	−41.3	−11.0	129.3	143.8	156.8	157.6
1-Br	−69.3	42.7	127.6	143.6	156.0	159.9
	−56.1	41.8	127.8	143.6	156.0	159.9
	−41.3	40.7	128.0	143.5	156.0	159.8
5-Cl	−67.8	39.0	94.3	146.2	150.2	160.7, 171.2
	−54.3	36.9	94.8	146.2	150.3	160.7, 171.3
	−36.0	33.7	95.4	146.0	150.2	160.4, 171.2
4-Cl[b]	−67.8	80.2	118.4	152.3	158.3	171.2
	−54.3	80.0	118.4	152.3	158.3	171.2
	−36.0	79.9	118.5	152.3	158.5	171.2
6-Cl[c]	−67	56.5		146.2		161.6
	−56	56.2		146.1		161.6

[a] Solutions are approximately 0.5 *M* in SO_2. [b] Previous values have been reported and are in agreement (ref 8). [c] Shifts of **7**-Cl are 139.0 and 145.1 ppm.

The variability of some of the shifts for **1**-Cl contrasts with the result for the parent tetramethylenechloronium ion **3**-Cl whose ^{13}C chemical shifts show no temperature dependence.[8] In this instance the carbonium ion formed by ring opening would be energetically unfavorable since it is primary. Between the extremes is 1-methyltetramethylenechloronium ion **4**-Cl[5] which could be in equilibrium with a secondary carbonium ion. Not surprisingly, we found that its

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

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

(7) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 6988 (1968).

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

^{13}C spectrum also showed essentially no temperature dependence (Table I).

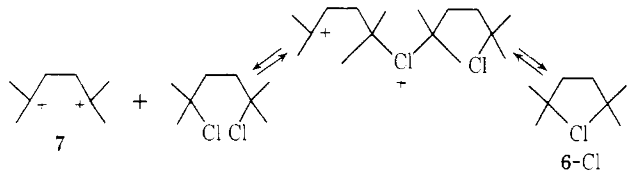
1,1,4-Trimethyltetramethylenechloronium ion (**5**-Cl) and 1,1,4,4-tetramethyltetramethylenechloronium ion (**6**-Cl) were prepared from 2,5-dichloro-2-methylhexane and 2,5-dichloro-2,5-dimethylhexane, respectively, as examples of ions whose equilibria might be influenced by the number of methyl groups present. Of particular interest is the observation of only one ^{1}H and ^{13}C nmr line for the nonequivalent geminal methyl groups in **5**-Cl (Tables I and II). This result, as well as the modest temperature dependence of ^{13}C shifts, suggests that equilibrium exists with a carbonium ion having equivalent methyl groups. The features of the nmr spectrum of 1,1,4,4-tetramethyltetramethylenehalonium ion were dependent on the identity of other species present, as outlined below. 1,1,4,4-Tetramethyltetramethylenechloronium ion (**6**-Cl) would logically be prepared from 2,5-dichloro-2,5-dimethylhexane, but a previous study indicated a dicarbonium ion **7** was obtained instead.[9] We found that the halonium ion **6**-Cl did form, however, when additional dichloride was added to the solution of **7**. A possible reaction pathway is shown in Scheme II.

Table II. ^{1}H Nmr Spectra of Halonium Ions[a]

Ion	$-CH_2X^+-$ or $-CHX^+-$	Other $-CH_2-$	CH_3
5-Cl	5.82[b]	2.88–2.61 m	1.77 d and 2.23 s
6-Cl		2.87 s	2.13 s
9-Cl	4.95 b and 6.24 b	3.0 to 1.7	1.02 t
9-Br	4.89 b[b] and 6.21 b	3.1 to 1.8 m	1.06 t
9-I	4.78 b[b] and 5.98 b	3.1 to 1.8 m	1.03 t

[a] All spectra taken on approximately 0.5 *M* solutions in SO_2 at −65°. Shifts measured relative to capillary TMS on both Varian A-60 and XL-100-15 instruments. [b] Band has two maxima which may be used by nonequivalent geminal protons.

Scheme II



When both the dicarbonium ion **7** and the halonium ion **6**-Cl were present in solution, the lines of each in the ^{1}H nmr spectrum were broadened, presumably due to an equilibrium between the two proceeding by a pathway such as is shown in Scheme III.

The ion 1,1-dimethyltetramethylenebromonium ion (**1**-Br) was prepared for the purpose of comparing the interaction of bromine and chlorine with a cationic center (*cf.* ref 10). The somewhat temperature dependent spectra of ions **5**-Cl, **6**-Cl, and **1**-Br (Table I and Figure 2) will be discussed later.

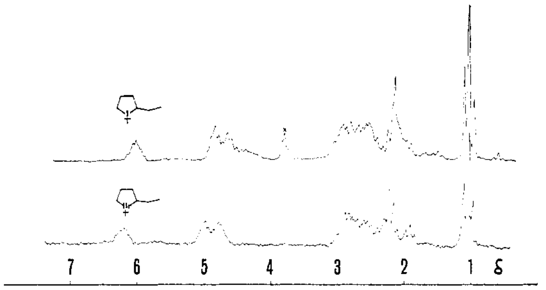
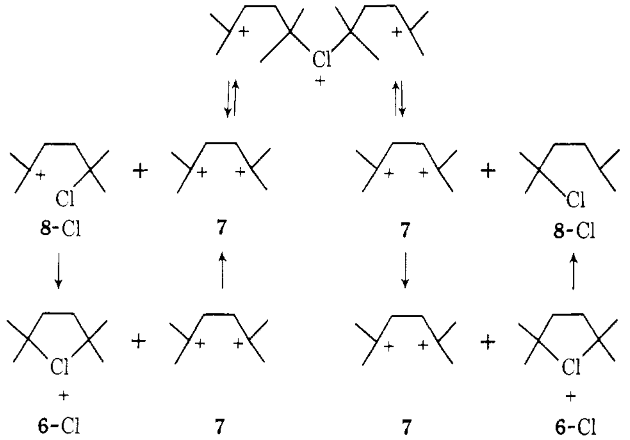


Figure 3. ^{1}H spectra at 100 MHz obtained at −65° for solutions produced by ionization of 1,6-diiodohexane and 1,6-dibromohexane in SbF_5–SO_2. The peak labelled X is due to an impurity which was present to different degrees in different samples.

Scheme III



Rearrangements in the Formation of Halonium Ions. The studies of equilibria discussed above developed from work on rearrangements of 1,6-dihalohexanes resulting from attempts at the synthesis of seven-membered ring halonium ions. As has been mentioned, the previously known formation of 1,1-dimethyltetramethylenechloronium ion (**1**-Cl) from 1,6-dichlorohexane[5] has been reinvestigated. However, we will defer presentation of the results for it in favor of the less complex ones for ionization of 1,6-dibromohexane and 1,6-diiodohexane in SbF_5–SO_2 solution.

The spectra obtained initially from 1,6-dibromohexane and 1,6-diiodohexane at −65° are shown in Figure 3. The large triplets at δ 1.06 suggest that 1-ethyltetramethylenehalonium ions **9**-Br and **9**-I were present. The identification of the ions was confirmed by the ^{13}C spectra (Table III) and by their reactions with methanol (see Experimental Section). As is shown in Scheme IV, the ethylated ions were found to be formed also by the reaction of CH_3F–SbF_5 adduct with 1,6-dihalohexanes (X-Br, I) or 1,5-dihalohexanes

Table III. ^{13}C Spectra of Ethyl Derivatives[a]

Ion	$-CHX-$ or $-CH_2X-$	Other $C-CH_2-C$	CH_3	CH_2 in CH_2CH_3
9-Cl	72.3 and 119.4	154.5 and 158.4[b]	180.0	169.9[b]
9-Br	77.9[c] and 125.3	152.0 and 156.9[b]	178.4[d]	162.1[b]
9-I	98.3 and 145.4	148.5[b] and 155.2[b]	175.8	161.0[b]

[a] See footnote *a*, Table I. Identification of multiplets was made by off-resonance decoupling. [b] Assignments are uncertain. [c] Doublet. [d] Quartet.

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(9) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

(10) Comparison data are available in ref 6, 11, and 12. It is relevant that six-membered ring iodonium and bromonium ions have been prepared but the chloronium ion has not (see ref 6) and that unsubstituted three-membered ring bromonium and iodonium ions formed but the chloronium ion did not (see ref 12).

(11) P. E. Peterson, *Accounts Chem. Res.*, **4**, 407 (1971).

(12) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).

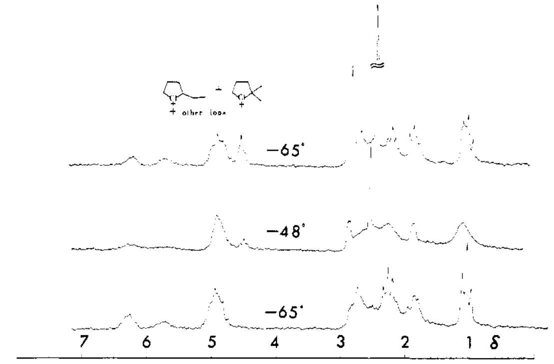
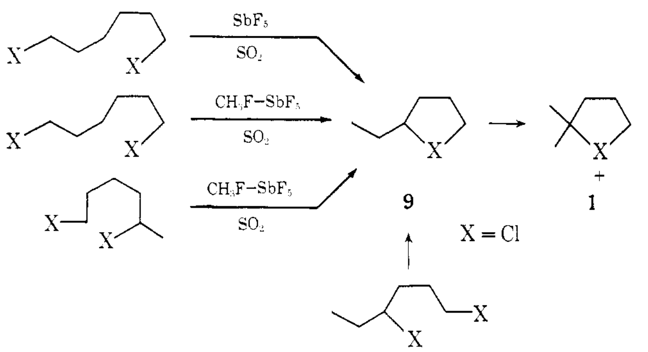


Figure 4. Temperature-dependent 100-MHz ^1H spectra produced by the solution of 1,6-dichlorohexane in SbF_5–SO_2.

Scheme IV



(X-Br, I). Seven- or six-membered rings were not observed, although the use of CH_3F–SbF_5 was shown to suppress rearrangements in the preparation of the parent six-membered ring bromonium and iodonium ions.[6]

As is also indicated in Scheme IV, 1-ethyltetramethylenebromonium ion (**9**-Br) rearranged to 1,1-dimethyltetramethylenebromonium ion (**1**-Br) upon standing for 1.25 hr at −27° or 7 weeks at −65°. The formation of 1,1-dimethyltetramethyleneiodonium ion (**1**-I) from **9**-I was not observed even when the sample was allowed to stand at room temperature for 1 hr, although a large amount of decomposition occurred.

When 1,6-dichlorohexane was carefully ionized with Dry Ice–acetone cooling and was rapidly transferred to the cold nmr probe, the spectrum shown in Figure 4 was obtained. Chemical shifts for the ^{13}C spectrum are shown in Table III. The presence of 1-ethyltetramethylenechloronium ion (**9**-Cl) is indicated. Unlike the spectra of **9**-Br and **9**-I, however, the spectrum of **9**-Cl was temperature dependent. As shown in Figure 4, when the temperature was raised from −65 to −48°, most of the lines broadened, and new lines which could be accounted for by 1,1-dimethyltetramethylenechloronium ion (**1**-Cl) appeared. If the solution was recooled to −65° before complete conversion to **1**-Cl had occurred, the sharp lines for **9**-Cl reappeared, along with those for **1**-Cl and some unidentified species having a possible methyl doublet underneath the upfield triplet. The temperature dependent spectrum of **9**-Cl also was observed when 1,4-dichlorohexane or 1,5-dichlorohexane was ionized in SbF_5–SO_2 solution (Scheme IV) or when 1,6-dichlorohexane reacted with CH_3F–SbF_5. The reaction of 1-ethyltetramethylenehalonium ions with methanol is described only in the Experimental Section. The tendency of the halo ethers to react during distillation, presumably owing to methoxyl participation processes, hindered our efforts to separate the products.

Interpretation of Nmr Data for Equilibrating Ions. Strong qualitative support for the carbonium ion–halonium ion equilibria postulated to exist for ions **1**-Cl, **5**-Cl, and **1**-Br is provided by the similarity of the patterns generated when values of $\Delta\delta$, the changes of ^{13}C chemical shift relative to shifts at the arbitrarily chosen lowest temperature, are plotted *vs.* temperature (Figure 2D). In all cases the conversion of C-4 from CXR^+ to CX upon opening of the halonium to carbonium ion as the temperature increases results, as expected, in an upfield shift which is smaller than the downfield shift at the potential cationic carbon C-1. The range of $\Delta\delta$ is contracted or expanded, depending in part on the amount of carbonium ion at equilibrium, but relative temperature effects at C-1 and C-4 are similar in all instances, confirming the common source for the temperature dependences of the chemical shifts. Later we shall show that the apparent linearity of the plots of Figure 2D is an artifact of the relatively narrow temperature range employed. Nevertheless, Figure 2D presents a convenient display of the raw nmr data. Quantitative interpretation of the data involves estimation of equilibrium constants from the previously used[2] equation, which involves values obtained at only one temperature

$$K = (\nu_{\text{obsd}} - \nu_{\text{h}})/(\nu_{\text{c}} - \nu_{\text{obsd}}) \qquad (1)$$

Here K = [carbonium ion (c)]/[halonium ion (h)], and ν designates the chemical shift of the nucleus used as a probe of the equilibrium position (C-1 or C-4 for ions **1** or **5**). Since the chemical shifts of the probe nucleus of the halonium ion and carbonium ion must themselves be estimated from those of model compounds, the probable accuracy of the K values is assessed from an intelligent guess of the error in the assumed chemical shifts. The most pessimistic viewpoint is that the estimated chemical shifts are subject to such large errors that even the qualitative demonstration *via* eq 1 of the presence of an equilibrium is subject to doubt. Fortunately the already discussed pattern of temperature dependence provides independent confirmation of an equilibrium.

In practice we believe that ±5 ppm is a reasonable estimate of errors in the estimated chemical shifts, based in part on the relative constancy[8] (±3 ppm) previously observed for ^{13}C chemical shifts of the groups CH_2Cl^+ or CH_2Br^+ in tetramethylenechloronium ions (five examples) or tetramethylenebromonium ions (three examples). The effect of methyl substituents on the chemical shifts of the closed ions must be taken into account. In previous work[8] it was found that the methyl group in 1-methyltetramethylenechloronium ion leads to a 35.3 ppm downfield shift at C-1. Shifts of this magnitude also occur upon methylation of the corresponding bromonium and iodonium ions.[8] The large shifts presumably reflect the large charge deficiency at C-1 in halonium ions. Subtracting 35.3 from the chemical shift of C-1 of 1-methyltetramethylenechloronium ion (**4**-Cl) (80.0 at −54.3°) gave our assumed value, 44.7 for the shift of C-1 on the closed ion **1**-Cl. It is possible that owing to the rather large magnitude of the methyl effect upon the chemical shift of C-1 in halonium ions our overall error in estimated chemical shifts is greater than ±5 ppm, as a referee suggests. Nevertheless, in order to obtain an indication of the effect of errors in chemical shift upon our estimates of ΔG, we assumed a ±5 ppm variation for purposes of calculation.

Appropriate comparisons with reference compounds led to a shift of 51.7 ppm for the tertiary carbon in the hypothetical closed 1,1-dimethyltetramethylenebromonium ion (**1**-Br). Previous work indicated that 1-methyl substituent caused an upfield shift of 3.0 ppm at the 4 carbon of halonium ions.[8] A shift for the 1 carbon of **5**-Cl was, therefore, calculated to be 47.7 ppm based upon the shift 44.7 of the 1 carbon in **1**-Cl. For the chemical shift of the cationic carbon of the carbonium ions **2**-Cl, **2**-Br, and **10**-Cl we used the value which we measured at −72° for the cationic carbon of *tert*-amyl cation, −141.3 ppm from CS_2 dissolved in SO_2 (internal CS_2). This value may be compared with Olah and White's value[4a] 139.2 (or 140.7 if the alternate referee preferred value mentioned in footnote 53 is used) from "CS_2 standard." The equilibrium constants and ΔG values which were found for the various systems based on these assumptions are given in Table IV.

Table IV. Equilibrium Constants and ΔG Values

Ion	Temp, °C	Equilibrium constant[a]	ΔG, kcal/mol
1-Cl	−69.3	0.31	0.48 ± 0.04
	−56.1	0.37	0.44
	−41.3	0.43	0.39
1-Br	−69.3	0.049	1.22 ± 0.27
	−56.1	0.054	1.26
	−41.3	0.060	1.29
5-Cl	−67.8	0.049	1.24 ± 0.20
	−54.3	0.062	1.22
	−36.0	0.081	1.19

[a] For the reaction halonium ion ⇄ carbonium ion.

Besides errors arising from estimation of chemical shifts the calculated values of K and ΔG values are subject to errors due to temperature measurement, traditionally a problem in nmr studies. We assessed these errors through temperature measurements with a calibrated copper–constantan thermocouple, as outlined below. To avoid repeated opening of tubes containing SO_2, we measured temperatures in a tube of ethanol in the nmr probe immediately prior to obtaining an nmr spectrum of an ion solution. In a control experiment a thermocouple in a tube of SO_2 gave readings 0.8–1.7° lower than values obtained in the ethanol tube. The error in our temperature measurements is accordingly assumed to be ±2°. All readings were taken with the decoupler on, since it gave increases in temperature of 0.8–1.7° in a control experiment. Measured variation within a tube were 0.6° (lower at bottom, compared to the middle of the solution) and 0.2° (noncentered *vs.* centered). In the spectrum of **1**-Cl at −69.3° the width of the line for the tertiary carbon is approximately 10 Hz, compared to 8 Hz for the other lines. From the 2 Hz difference and from the observed variation of chemical shift with temperature one may conclude that the combination of temperature differences in the signal producing portion of the tube and time variation of temperature during accumulation of the spectrum was only 0.2°. Since this value may represent a favorable case, it seems prudent to assume that variations may be several times this value. Nevertheless, our demonstration of limited temperature variation constitutes an important application of our novel temperature-dependent system.

The effect of the combined errors upon ΔG are given in Table V. The results are remarkably satisfactory, owing in part to the large range in ^{13}C chemical shifts used in the calculation. Because of their sensitivity to errors we have omitted ΔH and ΔS values and their error limits, but they are in the range 1 ± 1 kcal/mol and 0 ± 4 eu for the three compounds **1**-Cl, **1**-Br, and **5**-Cl.

Table V. Error Analysis for ΔG Values

			Errors due to			
Ion	Parameter, kcal/mol	Value	$\Delta\nu_h \pm 5$ ppm	$\Delta\nu_c$ ± 5 ppm	$\Delta\nu_{obsd}$ ± 0.2 ppm	Temp ± 2°
1-Cl	$\Delta G(-56.1)$	0.439	0.038	0.015	0.001	0.004
1-Br	$\Delta G(-56.1)$	1.258	0.267	0.012	0.008	0.012
5-Cl	$\Delta G(-54.3)$	1.217	0.194	0.012	0.004	0.012

The averaged chemical shifts in equilibrating systems should show a linear variation with the mole fraction, X, of one of the species in the system (eq 2). This relationship is illustrated in Figure 2A–C in which mole fractions of halonium ions, X_h, calculated from the equation $X_h = 1/(1 + K)$, are plotted *vs.* $\Delta\delta$. The mole fraction is thus seen to be the appropriate function of temperature to use in obtaining a theoretically linear plot *vs.* $\Delta\delta$. The explicit temperature dependence is readily obtained from the relationship of eq 3.

$$\nu_{obsd} = X_h[\nu_h - \nu_c] + \nu_c \qquad (2)$$

$$K = [e^{-\Delta H/RT}][e^{\Delta S/R}] \qquad (3)$$

Discussion of Equilibria and Rearrangements. We note that the ΔG values for halonium ion–carbonium ion equilibria (Table IV) are sensitive to the number of methyl substituents present and to the identity of the halogen. We first consider the methyl substituent effect, which increases the proportion of trimethylated cyclic halonium ion **5**-Cl in equilibrium with open carbonium ion. The effect, approximately 0.8 kcal upon ΔG, could result from destabilization of the open ion owing to conformational effects,[13] or to stabilization of the cyclic halonium ion possibly associated with electron donation from the methyl group to the ring.[14] The "*gem*-dimethyl effect" and other selective stabilizations of methylated cyclohexanes relative to the corresponding hexanes have been quantitatively accounted for by the number of gauche interactions in the various species considered, and by quantitatively estimated entropy effects.[11] However, the additional gauche interaction in the open carbonium ion in equilibrium with trimethylated cyclic chloronium ion **5**-Cl may be an interaction between chlorine and carbon, since the carbon chain may be extended into a zig-zag form. In 1-chloropropane the carbon–chlorine gauche inter-

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[13] N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).

[14] J. W. Larsen and A. V. Metzner, *J. Amer. Chem. Soc.*, **94**, 1614 (1972).

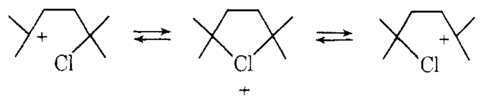
action is thought to be attractive[15] or at least nonrepulsive. Accordingly, it is not clear whether conformational effects can account for the increased proportion of ring closed **5**-Cl, compared to **1**-Cl.

It furthermore seems reasonable that the origin of the effect of methyl substitution may be related to that in three-membered ring halonium ions. For these ions Larson and Metzner found that successive substitution of methyl groups into the ring caused increases in stability of 5 kcal/mol in ΔH, relative to dihalide precursors.[14] The magnitude of the effect, along with evidence from nmr spectra, suggested that charge dispersal from methyl groups to the rings is an important source of the methyl group stabilization effect. Charge dispersal would be most pronounced when the methyl group is attached to the relatively electron deficient carbon, C-1. In view of this expectation, the previously reported rearrangement of 2-methyltetramethylenechloronium ion to the 1-methyl ion may be considered to support the role of charge dispersal by methyl groups.[16]

Whatever the origin of the methyl groups effect, it is of interest to consider its implications in the 1,1,4,4-tetramethyltetramethylenehalonium ion (**6**-Cl). The assumption of an additional 0.8 kcal/mol favoring the cyclic species, compared to the value for the equilibrium involving the trimethylated ion **5**-Cl, leads to the calculated value, 0.01, for the mole fraction of open carbonium ion present for the equilibrium involving **6**-Cl. Based on this result and estimated chemical shifts, the ^{13}C chemical shift observed for **6**-Cl would be only 0.71 ppm from that of the pure halonium ion.

The calculation mentioned above takes into account the circumstance that for the tetramethyl ion **6**-Cl three different chemical shifts for the tertiary carbons are averaged if the halonium ion is in equilibrium with a carbonium ion: that for the halonium ion, that for a tertiary carbonium ion, and that for a tertiary chloride as indicated in Scheme V. The tertiary chloride and tertiary carbonium ion shifts would have equal weight in the average since they both occur in the same ion so that effectively there would be an average of the shift of the tertiary carbon of the halonium ion with the average of the shifts of the other two types of carbon (−8 ppm). Thus, the effect of changes in chemical shift with temperature is smaller than for the other cases.

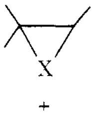
Scheme V



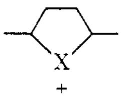
6-Cl

Turning to the effect of replacing Cl by Br, we note that the ΔG difference of 0.8 kcal corresponds to an increased proportion of the closed form in **1**-Br compared to that in **1**-Cl. Although the magnitude of the stability difference is remarkably small, it corresponds to previous qualitative observations to be mentioned below which have suggested the halonium ion stability order, iodonium > bromonium > chloronium.[10,11] In the present instance the stability is with respect to conversion to an open carbonium ion by formal breakage of two bonds from carbon to positively charged halogen and formation of one bond from carbon to uncharged halogen. Previously it has been noted that the rates of formation of five-membered ring halonium ions as transition states in neighboring group participation reactions are remarkably similar for halogens chlorine, bromine, and iodine, k_Δ for bromine participation being no more than threefold larger than that for chlorine participation.[11] The 0.8 kcal difference in ΔG observed in the present study corresponds to a fourfold rate preference for bromine participation at 25°. Accordingly, our measured ion stabilities adequately reflect earlier observations of transition-state stabilities, and the previous postulate[11] that halonium ion character is only minimally developed in the solvolysis transition states may be abandoned.

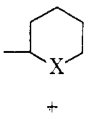
It is interesting that the parallelism between stable halonium ion energetics and solvolysis results seems to extend to three-membered rings. Results from the literature indicate that for these rings variation of the halogen causes relatively large energy differences, the stability order being I ≫ Br ≫ Cl. Solvolytic data in several solvents are cited in a recent review.[11] In the case of stable ions, attempted preparation of 1,1-dimethylethylenechloronium ion gave only open carbonium ion, as judged from hydrogen nmr spectra, whereas the bromonium and iodonium analogs appeared to exist wholly as the three-membered rings.[17] Although equilibrium constants are not known for these systems, the change in K owing to change from Cl to Br is obviously larger than that in the five-membered ring. Addition of a third methyl substituent makes the effect of changing halogen indiscernible since there is predominance of the closed three-membered ring even in the case (**11**-Cl) where the halogen is chlorine. It is of interest in comparison with the observations of the present study that the absence of temperature dependence of the ^{1}H chemical shifts of trimethylethylenehalonium ions **11**-Cl and **11**-Br was cited as evidence against equilibration of these ions with substantial concentrations of carbonium ions.[17] The apparent equivalence of *gem*-dimethyl groups, however, was suggestive of the presence of open carbonium ions in small amount. The observations in the present work that the *gem*-dimethyl groups in 1,1,4-trimethyltetramethylenechloronium ion (**5**-Cl) gave single ^{1}H and ^{13}C nmr peaks are likewise consistent with such an equilibrium. The methylene protons of methylethylenebromonium ion appear to be equivalent in the nmr spectrum although the same protons for methylethyleneiodonium ion clearly are not,[12] possibly as a result of substantial energy differences between the iodonium and bromonium ions. The methylene protons in β-bromo para-substituted cumyl cations were equivalent.[18] Studies of the effect of temperature on



11



12



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[15] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 15–16.

[16] P. E. Peterson and B. R. Bonazza, *J. Amer. Chem. Soc.*, **94**, 5017 (1972).

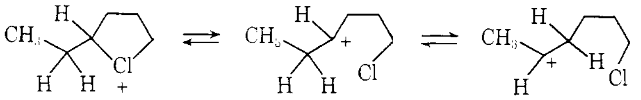
[17] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 947 (1968).

[18] (a) G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, **94**, 2044 (1972); (b) G. A. Olah, C. L. Jeuell, and A. M. White, *ibid.*, **91**, 3961 (1969).

the ^{13}C chemical shifts of each of these and other halonium ions might reveal whether apparent equivalencies are merely accidental or due to an equilibration between halonium ions and carbonium ions. Possible application of the method to other types of organic cations is mentioned in the Conclusion.

Both experimental[19] and theoretical[20] studies have shown the difference in stability of tertiary and secondary carbonium ions to be about 15 kcal/mol. Accordingly, it is not surprising that the chemical shifts of 1-methyltetramethylenechloronium ion (**4**-Cl) were almost insensitive to temperature as expected if no appreciable amounts of secondary carbonium ion are in equilibrium with the halonium ion. There is, nevertheless, some evidence that small amounts of a secondary carbonium ion might be in equilibrium with 1-ethyltetramethylenechloronium ion (**9**-Cl) since the lines in the ^1H nmr spectrum of that ion were subject to broadening with changes in temperature. Such broadening may be indicative of an exchange process occurring by hydride shifts in the carbonium ion as is shown in Scheme VI. In addition to the exchange shown in Scheme VI, hydride shifts involving hydrogens on the third carbon from chlorine may occur, but at a slower rate due to the inductive effect of the halogen. Note, therefore, that hydride shifts in 1-methyltetramethylenechloronium (**4**-Cl) would be less facile than ln 1-ethyltetramethylenechloronium ion (**9**-Cl). Olah and coworkers have observed a broadening in the spectrum of 1-methylethylenechloronium ion, however, which was also explained in terms of hydride shifts.[21] The amount of carbonium ion which would have to be in equilibrium with **9**-Cl to account for the broadening may be extremely small since Saunders and coworkers have found that hydride shifts for *sec*-butyl cation are fast on the nmr time scale even at −110°.[22] The rate of shift within the chloronium ion would be in the nmr range at the much higher temperatures used in the present work only if the equilibrium constant were so small as to compensate for the very fast rate of exchange in the carbonium ion. An alternative route for the exchange reaction could involve a protonated cyclopropane which would directly involve the methyl protons in the exchange.

Scheme VI

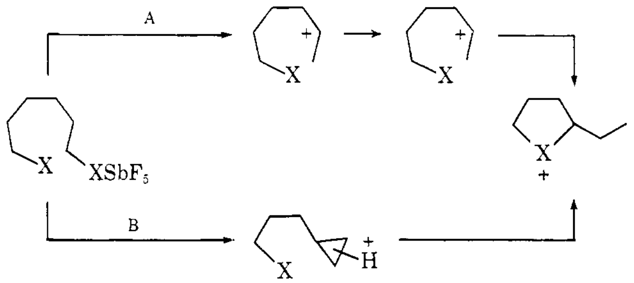


9-Cl

Part of the interest in the rearrangements reported in this paper was the possibility that seven-membered rings might be formed at least in part under some conditions from 1,6-dihalohexanes. The preparation of seven-membered ring halonium ions would be of interest in light of a recent theory that molecular orbital effects may give added stability to odd-membered ring halonium ions.[23] Since seven-membered rings were not formed in the reactions we studied, our results have only incidental bearing on the question of stability *vs.* ring size. Our results would have been obtained either if the observed rearrangement reactions occurred faster than formation of seven-membered rings or if first formed seven-membered rings rearranged to substituted five-membered rings. It is perhaps significant that rearrangement to six-membered rings was not detected (*cf.* following discussion of mechanisms).

At least two different mechanisms are possible for the formation of the 1-ethyltetramethylenehalonium ions **9** from 1,6-dihalohexanes. In one of them two successive hydride shifts occur following removal of halogen complexes to SbF_5 as shown in Scheme VII (path A). It is possible to formulate a mechanism involving a protonated cyclopropane (path B), however. Protonated cyclopropanes have, in fact, been considered as intermediates in the reaction of propyl chloride with $AlCl_3$[24] and in the hydride exchange reaction which has been observed for *sec*-butyl cation.[19] Successive 1,2-hydride shifts would, nevertheless, also accommodate the observation that the ethyl derivatives **9**-I and **9**-Br are formed from 1,5-dibromohexane and 1,5-diiodohexane. The most stable ion formed, at least for the chloronium and bromonium ions, was the 1,1-dimethyltetramethylenehalonium ion (**1**). Such an ion cannot be formed *via* simple hydride shifts but must result from rearrangement of the carbon skeleton itself. It is interesting to note that Olah and coworkers previously found that *cis*- and *trans*-1,2-dimethylethylenebromonium ions rearranged to 1,1-dimethylethylenebromonium ion.[12]

Scheme VII



The ethyl derivatives are not the only ions formed on ionization of 1,6-dihalohexanes although they do constitute the major initial products. That the minor components of the solutions contained methyl substituents is indicated by the peaks between δ 1.8 and 2.2 in Figures 3 and 4. Such methyl groups would be on carbon directly attached to positive halogen which would suggest ions such as **12** and **13**. It seems unlikely that the ions are **13**, however, in light of the failure of the direct preparation of such species. None of the chemical shifts in the present work agree exactly with those of the previous reports of either the cis or trans isomers of **12**,[25] but discrepancies in the chemical shifts of as much as 0.3 ppm in ^1H spectra of ions in SO_2 have been noted in this laboratory possibly due to differences in referencing procedures and/or positioning of the capillary within the nmr tube There were products in the reaction of the bromonium ion solution

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(19) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(20) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 5935 (1972).

(21) G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, **94**, 1164 (1972).

(22) M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, **90**, 6883 (1968).

(23) P. E. Peterson, *J. Org. Chem.*, **37**, 4180 (1972).

(24) (a) C. C. Lee and D. J. Woodcock, *J. Amer. Chem. Soc.*, **92**, 5992 (1970); (b) G. J. Karabatsos, J. L. Fry, and S. Meyerson, *ibid.*, **92**, 614 (1970).

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

with methanol which could have formed from **13**-Br. It is interesting to note that products consistent with the intermediacy of both **12**-Cl and **13**-Cl as well as **9**-Cl were detected in the trifluoroacetolysis of 6-chloro-1-hexyl nosylates.[26]

At least for the chloronium ion another species having a possible methyl doublet at δ 1.0 may be detected in the solution in which 1,1-dimethyltetramethylenechloronium ion (**1**-Cl) has partially formed. Such a methyl group must be at some other position than the carbon attached to halogen. Several such ions may be written, but the present data do not differentiate among them.

Conclusion

Although the focus of our own work continues to be cyclic halonium ions, searches for variable-temperature ^{13}C chemical shifts might also be valuable in the detection of equilibration between different positively charged ions of other types. For example, equilibration between different species has been considered for substituted cyclopropyl carbinyl cations[27] and for substituted norbornyl cations.[4b] Applications may also be made to systems in which other heteroatoms such as oxygen[28] are involved in bridging.

Experimental Section

Nmr Spectra. The ^1H spectra were obtained on both Varian A-60 and XL-100-15 instruments. For the ionic solutions chemical shifts were referenced to a capillary of TMS; internal TMS was used otherwise. The ^{13}C spectra were obtained on the Varian XL-100-15 instrument by the Fourier transform method with noise decoupling of protons and between 500 and 1000 pulses. The chemical shifts were measured relative to the central peak of CF_2BrCF_2Br contained in a 5-mm tube inside the 12-mm tube holding the sample. The shifts were referenced to internal CS_2 by the addition of 78.1 ppm.[8] External field-frequency lock was employed. Approximate temperature measurements were made with a thermometer inserted into a 12-mm tube containing ethanol or with a methanol sample for 5-mm tubes. Accurate temperature measurements were made with a copper–constantan thermocouple in a 12-mm tube containing ethanol.

The upper limit in the temperature used for the variable-temperature ^{13}C chemical shifts was determined by the fact that the tertiary carbons became increasingly difficult to see without long pulse delays. The lower limit was determined by the freezing point of sulfur dioxide (−72.7°).

Ionic Solutions. The chloronium ion solutions were formed in 5-mm nmr tubes by the addition of 0.00025 mol of the appropriate dichloride to 0.5 ml of a 1.25 *M* solution of SbF_5 in SO_2 (0.00063 mol of SbF_5). The solutions were stirred with a nichrome wire while they were cooled in a Dry Ice–acetone bath, and the spectra were obtained immediately. Similar proportions were used in the preparation of ^{13}C nmr samples in 12-mm tubes. The rearrangements leading to 1,1-dimethyltetramethylenechloronium ion (**1**-Cl) went to completion when samples were allowed to stand at −65° in a freezer overnight.

Solutions of the ions from 1,6-dibromohexane and 1,6-diiodohexane were made at concentrations of 0.5 *M* in volumetric flasks with 2.5 mol of SbF_5 to 1.0 mol of the dihalide. Nmr samples were taken with a cooled pipet when the solids which formed had settled.

Partial formation of 1,1-dimethyltetramethylenebromonium ion (**1**-Br) from the solution produced from 1,6-dibromohexane could be accomplished when the sample of the solution was held at −27° for 1.25 hr in the nmr spectrometer. Almost complete rearrangement occurred when the sample remained for 4 hr in a low-temperature bath at −18°. The solution produced from 1,6-diiodohexane showed only slight changes after the sample had remained at −18° for 46 hr. After a sealed nmr tube of it had remained 1 hr at room temperature, there was a very dark red color (iodine?) and much reduced peaks for the ions in the nmr spectrum. Ionic solutions were prepared in several cases (see text) by the addition of the appropriate dihalide precursor to a solution of CH_3F-SbF_5 adduct in SO_2 as has been previously described.[6]

Reactions of Ionic Solutions with Methanol. Ionic solutions were poured into approximately double volumes of methanol which had been prechilled to −65° and which contained about 10% by weight K_2CO_3. The temperature was monitored during the addition and was not allowed to rise above −30°. After addition of the SO_2 solution was complete, the solutions were allowed to warm to room temperature, then were poured onto water and extracted with CCl_4. The CCl_4 solution was then washed once with water and dried.

A solution made from 1,6-dichlorohexane was quenched immediately. The ^1H nmr spectrum indicated several products were formed: δ 5.3 m (olefin), 3.43 t (CH_2Cl or CH_2OMe), 3.21 s (1 or 2° OCH_3), 3.07 s (3° OCH_3), 2.3–1.3 m ($-CH_2-$), 1.10 s (CH_3), and 0.95 m (CH_3). Only a partial separation of products was achieved by distillation. From the solution produced from 1,6-diiodohexane was produced a mixture giving the following nmr spectrum: δ 3.22 s (OCH_3), 3.24 m (CH_2I?), 2.0–1.2 b ($-CH_2-$), 1.2–0.85 (CH_3).

The products from reaction of methanol with a 70:30 mixture of **9**-Br and **1**-Br were distilled at 5 mm (platinum band) to give fractions boiling principally in the following ranges: 44–48° (0.31 g); 56–58° (0.46 g); 75–80° (2.24 g); above 80° (0.52 g). The pressure was lowered to 0.5 mm to give 2.56 g of material above 50°. There was also 1.75 g of material with intermediate boiling points. The fractions were analyzed by vpc on a glass column of DC-550 silicone oil (Hewlett-Packard 5750 with flame detector, 162°) and by nmr spectroscopy.

The 44–48°-fraction was characterized by an nmr band between δ 5.07 and 5.55 and a multiplet in the range δ 1.12–0.97 and, thus, was identified as olefinic material containing methyl groups. The second fraction had a similar nmr spectrum, and the vpc retention times of both were the same (largest peaks 1.8 and 2.0 min). The ^1H nmr spectrum of the 75–80° fraction was as follows: δ 3.38 t, 3.25 s, 3.11 s, 3.07 p, 2.00–1.35 m, 1.13 s, and 0.89 t. The use of the shift reagent $Eu(fod)_3$ confirmed the multiplicity of the lower field peaks. It was concluded that the solution was primarily 1-bromo-4-methoxyhexane, the expected product of reaction of 1-ethyltetramethylenebromonium ion (**9**-Br). The principal ^{13}C resonances (measured from internal CS_2) were 111.4, 136.1, 159.6, 160.6, 163.6, 166.4, and 182.8 ppm, which are consistent with 1-bromo-4-methoxyhexane. The higher boiling fractions had many peaks in the region δ 3.90–3.20 and may be dibromides and/or alcohols. In another methanol quench experiment, alkenes apparently were formed by decomposition upon distillation.

Halonium Ion Precursors. Where possible the dihalides were obtained from commercial sources as follows: 1,6-dibromohexane and 1,6-diiodohexane (Columbia Organics); 1,6-dichlorohexane (Eastman). Other compounds were made as indicated.

1,5-Dibromohexane was synthesized from *N*-benzoyl-2-methylpiperidine through the action of phosphorus tribromide and bromine in a procedure which has been described.[29] The benzonitrile side product was removed by extraction eight times with concentrated H_2SO_4, and the product was distilled at 4.0 mm to give a 35% yield of compound boiling between 83 and 86° (lit.[29] bp 120–122° (20–25 mm)). A side product which was higher boiling may be a tribromide produced by elimination of HBr and addition of Br_2; ^1H nmr spectrum of main product: δ 4.00 p (1.6), 3.32 t (3.7), 2.1–1.5 b, and 1.68 d (17.1); ^{13}C spectrum 142.6, 151.9, 159.8, 160.0, and 165.7 (2 peaks). *Anal.* (Bernhardt, Germany) Calcd for $C_{16}H_{12}Br_2$: C, 29.54; H, 4.96. Found: C, 29.57; H, 4.82.

1,5-Diiodohexane. The compound 5-hexen-2-ol (produced by reduction of allylacetone,[30] 30.0 g, 0.3 mol) was dissolved in 30 ml of pyridine, and the solution was cooled in ice. To it was added a cooled solution (114.6 g, 0.6 mol) of *p*-toluenesulfonyl chloride (Eastman) in 80 ml of pyridine, and the solution was left at about 5° for 20 hr. Water was added dropwise with cooling in ice until

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

(27) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972).

(28) (a) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972); (b) G. A. Olah and P. J. Szilagyi, *J. Org. Chem.*, **36**, 1121 (1971).

(29) A. W. Dawkins and T. P. C. Mulholland, *J. Chem. Soc.*, 2203 (1959).

(30) G. Allen, Ph.D. Thesis, St. Louis University, 1963.

heat was no longer evolved, then the mixture was poured into 350 ml of water which was extracted with ether. The ether solutions were washed with 3 *N* HCl, saturated $NaHCO_3$solution, and water and were dried over $MgSO_4$. Removal of solvent gave 72.2 g of product (0.28 mol, 94%).

To the tosylate was added 300 ml of reagent grade acetone and 72.2 g of NaI, and the mixture was stirred at reflux for 4 hr. The mixture was then poured into 250 ml of water, which was extracted four times with ether. The combined ether solutions were washed once with 50 ml of saturated sodium thiosulfate solution and then with 50 ml of water and were dried over $MgSO_4$. Distillation (spinning band) gave 43.0 g of material boiling at 75° (33 mm).

Production of the diiodide was accomplished by a recent modification of the hydroboration reaction.[31] About 100 ml of freshly distilled tetrahydrofuran was cooled with ice in a three-necked flask flushed with nitrogen. To the flask was added, through a rubber septum, 165 ml of diborane in tetrahydrofuran (Alfa, 165 mmol) and then 34.65 g of 2-methyl-2-butene (330 mmol) with cooling in ice. The solution was stirred at room temperature for 1 hr, and 31.5 g of the 5-iodo-1-hexene was added dropwise with cooling. After 3 hr at room temperature 41.9 g of I_2 (165 mmol) was added followed by 55 ml of 3 *N* NaOH in methanol (165 mmol). The flask was then cooled, and a mixture of 25 ml of 3 *N* NaOH and 25 ml of 30% H_2O_2 was added to destroy remaining alkylboranes. The aqueous solution was extracted three times with 100-ml portions of CH_2Cl_2 which was washed with 30 ml of saturated $Na_2S_2O_3$ solution and dried with Na_2SO_4.

The diodide could not be completely separated from the side product 2-methyl-3-butanol by distillation, so the alcohol was converted to ketone by Brown oxidation. The product was distilled to give 14.6 g (29%) of 1,5-diiodohexane boiling at 100° (1.2 mm) (spinning-band distillation): nmr δ 4.02 p (1.9), 3.12 t (4.4), 1.90 d overlapping a broad peak centered at 1.67 (19.6 together); ^{13}C spectrum 150.4, 159.6, 161.4, 163.1, 164.2, and 186.8. *Anal.* (Bernhardt) Calcd for $C_6H_{12}I_2$: C, 21.32; H, 3.58. Found: C, 21.59; H, 3.10.

1,4-Dichlorohexane. A total of 20.04 g (200 mmol, Chemical Samples) of 5-hexen-3-ol was added dropwise to a solution of 46.2 ml (440 mmol) of 2-methyl-2-butene (Aldrich) to which had been added 44 ml (440 mmol, Callery) of BH_3–$S(CH_3)_2$ at 0°. A gas evolved during the addition. The solution was stirred 3 hr at 0–10°, then a mixture of 60 ml of 3 *N* NaOH and 60 ml of 30% H_2O_2 was added at 0°, and then the solution was allowed to warm to room temperature. Water was added; the solution was filtered; and then it was extracted continuously with diethyl ether for 10 hr. The ether solution was dried overnight with Na_2SO_4 and then distilled (spinning band, 47–55° (0.075 mm)) to give a very viscous liquid.

To the distillate was added 32.17 ml (407 mmol) of pyridine and then 47.6 g (400 mmol) of thionyl chloride while it was cooled in ice. The mixture was heated to 100° until evolution of gas ceased (about 2 hr). The tarry mixture was washed with methylene chloride which was then filtered through a bed of Celite, washed twice with 10% HCl and then once with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. The dried solution was distilled to give 0.99 g of product which was 75% pure to vpc and 2.06 g of pure compound (7% yield from olefin): bp 48° (2.0 mm); nmr δ 4.75 p, 4.51 t, 2.05–1.05 m, 1.07 t. *Anal.* (Galbraith Laboratories, Knoxville, Tenn.): Calcd for $C_6H_{12}Cl_2$: C, 46.47; H, 7.80. Found: C, 46.85; H, 7.94.

2,5-Dichloro-2-methylhexane. In a 1000-ml three-necked flask was placed 35.0 g (0.35 mol) of γ-valerolactone (Columbia) and 500 ml of anhydrous ethanol. Hydrogen chloride was bubbled through the solution for 4 hr, then 250 ml of water was added. The aqueous solution was extracted five times with CH_2Cl_2, which was then dried and distilled to give 34.8 g of material boiling at 83° (12 mm) (spinning-band distillation). Nmr of product (δ 4.02 q, 3.38 t, 2.34 m, 1.95 m, 1.52 d, and 1.22 t) is consistent with ethyl 4-chlorovalerate. An impurity (about 15%) partially codistilled.

A 500-ml flask was flushed with N_2 and 7.31 g (0.300 mol, MCB for Grignard) of magnesium and 100 ml of anhydrous diethyl ether were placed in it. A small portion of 42.6 g (0.300 mol) of methyl iodide in 50 ml of ether was added. Then the remaining methyl iodide was added while the flask was cooled in ice. A total of 20.6 g of the chloro ester from above was added dropwise while the solution was cooled in ice, and the solution was heated on a steam bath for 1 hr. The reaction mixture was again cooled and enough saturated ammonium chloride solution added to precipitate the magnesium salts (about 40 ml). The precipitate was washed several times with ether and solvent was removed by distillation. The crude product was used for the next step.

The product of the Grignard reaction was stirred with 100 ml of concentrated HCl for 1 hr. The acid was extracted three times with ether. The combined organic solutions were washed once with saturated $NaHCO_3$ solution and once with saturated $Na_2S_2O_3$ solution and dried over molecular sieves (4A). The resulting solution was distilled (spinning band) to give 12.1 g of a liquid boiling at 80° (17 mm) (about 56% overall): nmr δ 3.92 b, 1.90 b, 1.59 s, 1.50 d, 1.1 (trace impurity). *Anal.* (redistilled products, Bernhardt): Calcd for $C_7H_{14}Cl_2$: C, 49.72; H, 8.35. Found: C, 50.32; H, 8.29.

2,5-Dichloro-2,5-dimethylhexane resulted from treatment of 2,5-dihydroxy-2,5-dimethylhexane (Aldrich) with concentrated HCl. Recrystallization from hexane gave white needles: mp 65–67° (uncor) (lit.[32] mp 64°); nmr δ 1.90 s and 1.55 s.

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