Proton and Carbon-13 Nuclear Magnetic Resonance Spectra of Equilibrating Organic Cations. Evidence for a Six-Membered-Ring Halonium Ion in Equilibrium with a Tertiary Carbonium Ion

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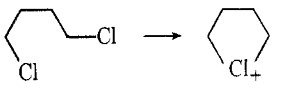
1,7-Dichloroheptane, 1,5-dichloro-5-methylhexane, and 1,4-dichloro-4-methylhexane ionized in SbF_5–SO_2 solution at −78° to give a mixture consisting principally of the following cyclic chloronium ions in equilibrium with appropriate tertiary carbonium ions: 1,1-dimethylpentamethylenechloronium ion, 1-methyl-1-ethyltetramethylenechloronium ion, and 1,1,4-trimethyltetramethylenechloronium ion. With time or higher temperatures the NMR spectrum indicated conversion of the mixture of ionic species into 1,1,4-trimethyltetramethylenechloronium ion. The three equilibrium constants for the reaction halonium ion $\rightleftarrows$ carbonium ion were 6.8 ± 2.0, 0.53 ± 0.07, and 0.055 ± 0.027, respectively, at −59.7° as determined by ^{13}C NMR chemical shifts. These results show that the six-membered-ring chloronium ion is predominantly converted to open carbonium ion at equilibrium, whereas five-membered chloronium ions exist predominantly as the cyclic species. The energy and entropy terms which may account for these results are discussed.

In previous work[2] the following reactions (eq 1–3) of polymethylenedihalides with SbF_5 in SO_2 have been observed. The ion 4 is presumably formed from 1,4-dichloropentane (3) in a process involving hydrogen shift, whereas hydrogen and carbon shifts are involved in the formation of 6 from 1,5-dichloropentane.



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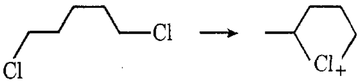

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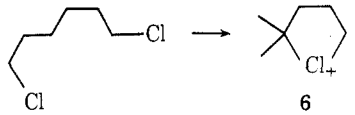
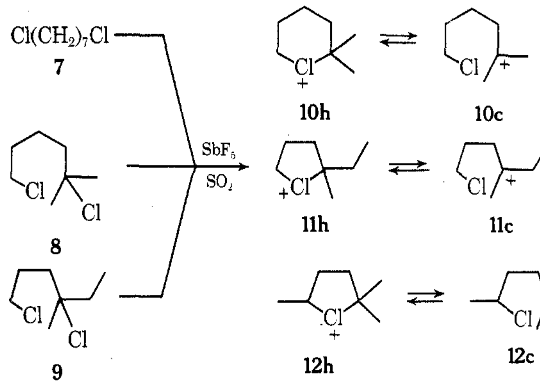


5 6 (3)

We have now studied the products of reaction of the next member of the series, 1,7-dichloroheptane (7). In contrast with the clean reactions of dihalides 1, 3, and 5, the reaction of 1,7-dichloroheptane produced a complex ^1H NMR spectrum (Figure 1) in which some of the chemical shifts were not readily attributable to known types of halonium or carbonium ion. Both the relative amounts and *positions* of some of the peaks seemed to vary from experiment to experiment. Below we shall describe observations which indicate that the rapidly equilibrating carbonium ion–halonium ion systems, **10h** $\rightleftarrows$ **10c** and **11h** $\rightleftarrows$ **11c**, sometimes accompanied by **12h** $\rightleftarrows$ **12c**, were the major products present. As we shall point out again, still unidentified components also were formed in some experiments. As shown in Scheme I, the products, **10**, **11**, and **12** were obtained also upon ionization of the branched dihalides **8** and **9**. Temperature dependence of the equilibrium constants and slow conversion of the ions to the most stable equilibrating system, **12h** $\rightleftarrows$ **12c**, were responsible for the apparently variable results of early experiments. (The letters **h** and **c** designate halonium and carbonium ion forms, respectively). Comparable rapid equilibria between halonium ions and carbonium ions have previously been reported in the case of five-membered-ring chloronium ions.[3a] Although six-membered-ring iodonium and bromonium ions were previously reported,[4] there has been no previous NMR detection of a six-membered-ring chloronium ion.

Scheme I



Results

Both the ^1H and the ^{13}C spectra of the ionized solutions obtained from 1,7-dichloroheptane were complex (Figures 1 and 2, Tables I and II). Nevertheless, the ^{13}C spectrum clearly indicated the presence of three seven-carbon ions or equilibrating groups of ions. The most notable features of the hydrogen spectrum (approximately −65°) were an apparent triplet at δ 3.43 showing the unusually small J value 4 Hz and an upfield triplet at δ 1.19, J = 7 Hz. The appearance of the downfield triplet is reminiscent of the spectrum of the *gem*-dimethyl group of the *tert*-amyl cation,[5] which shows long-range coupling (J = 5 Hz), However, the chemical shift, δ 3.43, is substantially upfield from that of *tert*-amyl cation (δ 4.12). An equilibrating mixture of **10d** and a lesser amount of **10h** is, however, consistent with our observations. The triplet at δ 3.75 also is in an appropriate position for the CH_2Cl methylene hydrogens in **10c** $\rightleftarrows$ **10h.** More definitive evidence for the presence of the structure **10c** $\rightleftarrows$ **10h** is provided by ^{13}C NMR spectroscopy and quenching experiments, to be described.

That the second species present in the mixture contained an ethyl group was suggested by the presence of the previously mentioned triplet at δ 1.19. The structure **11h** $\rightleftarrows$ **11c**, equilibrating ions with the halonium ion form predominating, are reasonable possibilities. As expected, if a small amount of the carbonium ion form contributes to the averaged spectrum, the assigned methyl resonance, at δ 2.53 (Figure 1) shows significant broadening, attributable to

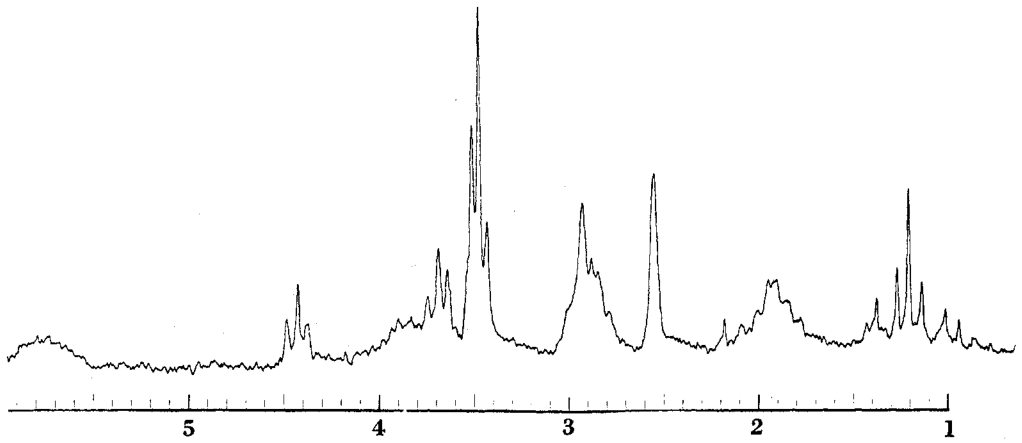


Figure 1. ^{1}H NMR spectrum of the mixture of ions **10**, **11**, and **12** in SbF_5–SO_2 solution.

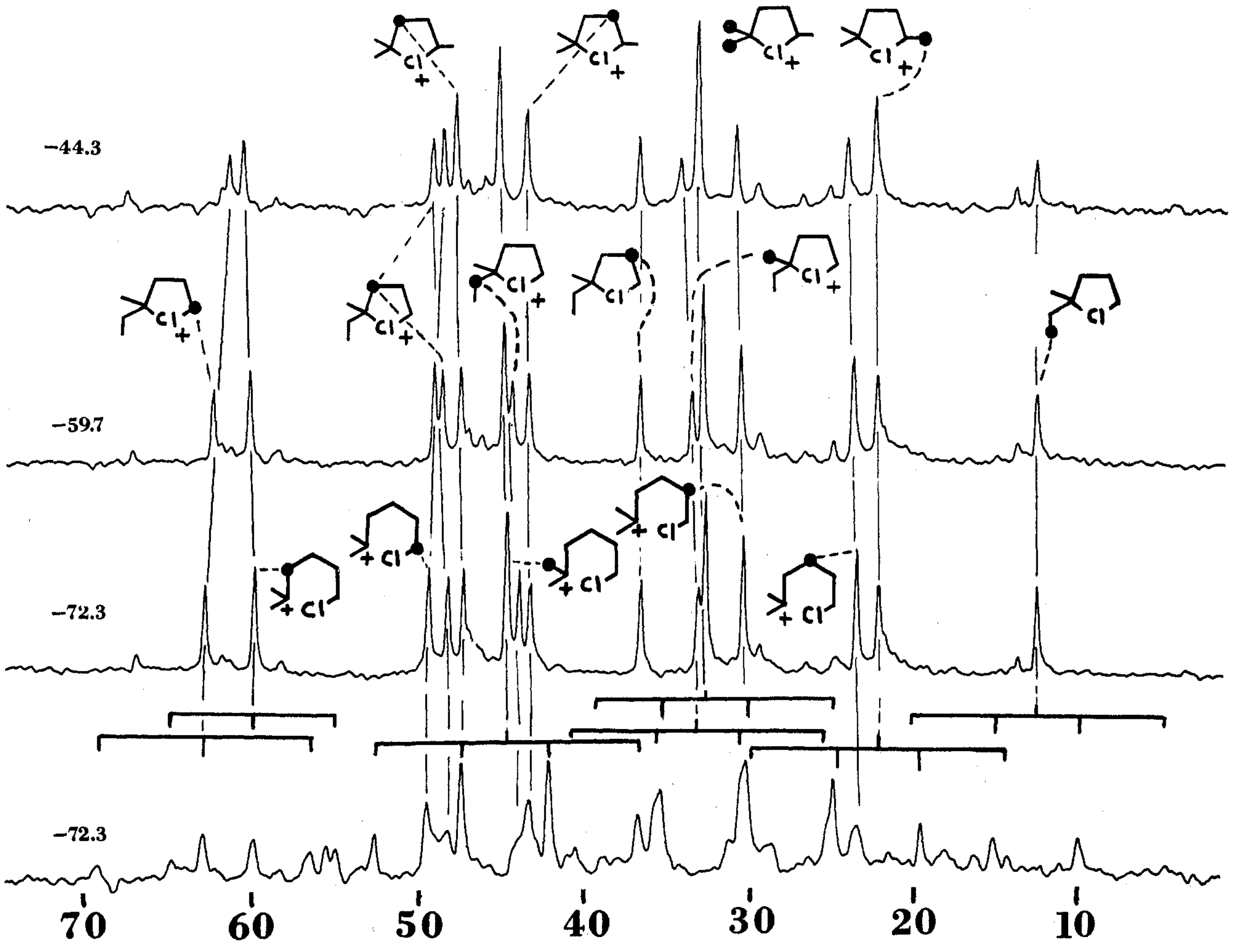


Figure 2. Variable-temperature ^{13}C NMR spectra of the mixture of ions **10**, **11**, and **12**.

long-range coupling. However, spectra taken at high temperatures showed a partially resolved unassigned second peak in this region. The triplet at δ 4.42 (Figure 1) is attributable to the CH_2Cl^+ methylene hydrogens in **11**. Additional evidence for the presence of **11h** ⇄ **11c** was provided by ^{13}C NMR and quenching experiments, to be described.

The third species, **12** (Scheme I), was present only in small amounts immediately following ionization of **7** at −78°, as indicated by the small size of its singlet at δ 2.2 (Figure 1). However, the spectrum of **12**, which was known from previous work,[3] became the dominant feature a sample of which was stored overnight at −65°. The identification of **12**, confirmed by ^{13}C NMR and quenching experiments, simplified the spectroscopic studies of ion mixtures, since allowing for the presence of **12** (if present) in effect reduced the structural problem to that of a two-component mixture. In addition to the features of the hydrogen spectra of ion mixtures which have been described, additional unassigned peaks were present in some of the ion mixtures, including those shown near δ 5.75 in Figure 1, downfield peaks in the region δ 8.5–10, and lines at δ 3.76 and 4.27 (not present in Figure 1).

During ^{13}C NMR experiments, peaks for **12** increased irreversibly, especially at higher temperatures. After allowing for these peaks, the upfield region still showed considerable complexity (Figure 2). A striking feature is that a

Table I
^1H NMR Spectra of Equilibrating Ions

Ions	$-CH_2Cl^+-$ or CHCl	$-CH_3$
10h and **10c**	~4.4 t[a]	3.43 t
11h and **11c**	4.32 t	2.63 s and 1.20 t
12h and **12c**	6.55 m	2.19 s and 1.85 d

[a] Temperature dependent.

Table II
^{13}C NMR Chemical Shifts of Equilibrating Ions

Ions	Temp, °C	$C-X^+$[a]	$C-CH_2C$[a]	CH_3[a]
10h ⇌ **10c**	−72.1	49.1, 309.3	23.3, 30.2, 61.6	44.4
	−59.7	48.7, 310.9	23.4, 30.3, 59.9	44.6
	−44.3	48.0, 313.5	23.7, 30.4, 60.2	44.7
11h ⇌ **11c**	−72.1	62.7, 213.1[b]	36.3, 43.6, 48.0	12.4, 32.9
	−59.7	62.1, 219.3	36.2, 44.1, 48.2	12.3, 33.2
	−44.3	61.0, 226.2	36.2, 44.7, 48.7	12.2, 33.8
12h ⇌ **12c**	−72.1	99.2, 154.1	43.0, 47.1	22.0, 32.4
	−59.7	98.9, 155.6	43.1, 47.1	22.0, 32.5
	−44.3	98.3, 158.4	43.0, 47.3	21.9, 32.7

[a] For tentative assignment see Figure 2. [b] Measured at −72.3°

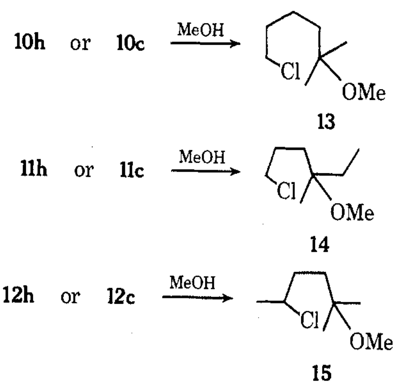
number of the frequencies were temperature dependent, some shifting upfield with increasing temperature whereas others shift downfield. Spectra taken at five temperatures (three shown in Figure 2) showed that some peaks reversed their relative positions as the temperature was changed. The temperature dependence provides strong evidence that equilibrating halonium–carbonium ion systems are present, by analogy with the systems which we previously studied.[3a] As in the earlier study the lines which shifted downfield with increasing temperature were assigned to carbons near the carbonium ion center, whereas those which shifted upfield were assigned to carbon atoms in the vicinity of the primary chlorine in the carbonium ion, as expected if the percentage of carbonium ion increases with temperature. The coupled spectrum (Figure 2) served to distinguish CH_2 carbons from others. Based on the features mentioned above, plus comparison of chemical shifts with those from our earlier papers, a tentative assignment (Figure 2) was made for all major lines. Although our ability to find peaks in the expected regions which exhibit the expected temperature dependence provides additional evidence for the presence of structures **10** and **11**, the most useful information gained from the ^{13}C NMR spectrum is the evidence (from temperature dependence) that equilibrating systems were present. As in the earlier study, the chemical shifts of the tertiary carbons, which were especially temperature dependent, were used in the calculation of equilibrium constants (see below).

Although we postulated the identity of ions **10**, **11**, and **12** from NMR studies, reaction of the ion solution with methanol to give ethers **13**, **14**, and **15** (Scheme II) provided probably the most unequivocal evidence for the presence of structures **10** and **11**. The ^1H and ^{13}C NMR spectra of the products corresponded with those of compounds prepared by methanolysis of the corresponding tertiary dichlorides (cf. Scheme II). The extraordinary power of ^{13}C NMR spectroscopy for identification of mixtures was illustrated by examination of distillation fraction containing **13**, **14**, and **15**. Both the presence of these ethers and the absence of others in appreciable amounts was demonstrated, although some lower boiling alkenes were present in some fractions.

1,5-Dibromo-5-methylhexane, the bromine analogue of **8**, also ionized in SbF_5–SO_2 solution at −78° to give a solution whose ^1H and ^{13}C NMR spectra were consistent with the presence of a six-membered-ring ion analogous to **10h** in equilibrium with a smaller amount of the carbonium ion analogous to **10c**. Other species were present, probably including an ethylated ion analogous to **11**. However, 1,5-dibromo-5-methylhexane was difficult to purify as it decomposed badly on distillation, and no detailed work was done with the slightly impure material available.

Calculations. Equilibrium constants for the reaction cyclic halonium ⇄ carbonium ion were calculated by the previously described method[3] from the chemical shifts of the tertiary carbons in **10**, **11**, and **12** with the equation $K = (\nu_h - \nu_0)/(\nu_0 - \nu_c)$ where ν_h = chemical shift of the halonium ion, ν_c = chemical shift of the carbonium ion, and ν_0 = the observed averaged chemical shift. Chemical shifts in parts per million from Me_4Si were estimated as follows. For **10c** and **12c** the shift of the tertiary carbon was assumed to be the same as that of *tert*-amyl cation, 334.7 ppm.[3] For **11c** the value 338.5 ppm was used. The shift of 148.7 ppm, which was previously used for the tertiary carbon in 1,1-dimethyltetramethylenechloronium ion, was used for **10h** even though there is an obvious risk in assuming that corresponding carbons in five- and six-membered rings have the same chemical shift. The chemical shifts of the 1 carbons in tetramethyleneiodonium ion and pentamethyleneiodonium, for example, differ by 13.1 ppm.[3] The difference for the corresponding bromonium ions is only 7.5 ppm, however, so that it is reasonable that a negligible difference occurs for chloronium ions.

Scheme II



The shift of the tertiary carbon in **11h** was taken to be 156.4 ppm based on the previously measured shift of the 1 carbon in 1-ethyltetramethylenechloronium ion, 121.1 ppm, and the observed downfield shift of 35.3 ppm caused by a 1-methyl substituted on the carbon to which it is attached. As before,[3] a shift of 145.7 ppm was used for the tertiary carbon in **12h**.

From the assumed and observed chemical shifts the equilibrium constants and free-energy differences shown in Table III were computed. The errors shown are based on an error of ±0.01 ppm in the measured chemical shifts, ±2° in

Table III
Equilibrium Constants and ΔG Values for Halonium Ion–Carbonium Ion Equilibria

Ion	Temp, °C	Equilibrium constant	ΔG, kcal/mol
10	−44.3	7.9	−0.93
	−59.7	6.8 ± 2.0	−0.82 ± 0.1
	−72.3	6.3	−0.73
11	−44.3	0.62	0.22
	−59.7	0.53 ± 0.07	0.27 ± 0.05
	−71.8	0.45	0.32
12	−36.0	0.081[a]	1.19[a]
	−44.3	0.072	1.20 ± 0.2
	−54.3	0.061[a]	1.22
	−59.7	0.055 ± 0.03	1.23 ± 0.2
	−67.8	0.049[a]	1.24[a]
	−72.3	0.046	1.23

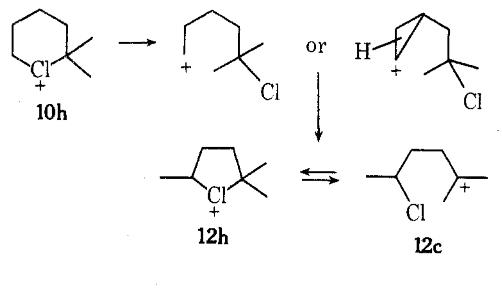
[a] From ref 2.

the temperature and ±5 ppm in the assumed chemical shifts. Although the latter value (±5 ppm) was used as a basis of calculation, a larger value (±10 ppm) would not affect our conclusions or discussion. Referees have expressed some skepticism regarding the reliability and accuracy of our calculations because of the assumptions involved. Let us consider in more detail the data for ion **10**. The observed tertiary carbon shift (approximately 310 at −60°) is 24 ppm from the estimated values for the tertiary cation (334.7) and enormously far from that of the chloronium ion (148.7). The open cation **10c** differs from the *tert*-amyl cation only in having attached carbons at the γ and δ positions, plus a chlorine at the ϵ position. The average shift produced by a γ carbon is only −2.5 ppm, and δ and ϵ effects are usually much less. Our assumed error is based on consideration of these values. Since the ^{1}H NMR spectrum indicates that a *predominantly open* cation such as **10c** is present, and since **11c** is expected to be predominantly closed based on our earlier work, there is little reason to doubt that the temperature-dependent peak near 310 ppm is that of **10c**. In summary, we have cited what appears to us to be a sound basis for our calculations and conclusions, although evidence presently unknown to us could lead to a modification of our interpretation.

Discussion

It is interesting that the dimethylated six-membered-ring chloronium ion **10h** has now been observed as a component of an equilibrating system. Its rearrangement reaction (Scheme III) involving the breaking of the bond between chlorine and the unmethylated carbon (to give a primary carbonium ion or its protonated cyclopropane equivalent) is relatively slow. In contrast, the unsubstituted six-membered-ring chloronium ion apparently rearranged too rapidly to allow its preparation.[3] This inference is based on the observation that the corresponding iodonium ion was relatively stable whereas the six-membered-ring bromonium ion rearranged fairly rapidly.[3] Although the primary cationic transition states for rearrangement of unsubstituted and dimethylated chloronium ion should be of similar stability, the presumed difference in rates of rearrangement can be understood in terms of ground-state stabilization of the dimethylated reactant, **10h.** Substantial stabilization of three-membered-ring halonium ions by methyl substituents has been observed, and smaller stabilization of larger rings has been suggested.[4,6] We note that this stabilization, if present, slows but does not prevent rearrangement of **10** to trimethylated ion **12** (Scheme III) at higher temperature or longer reaction times.

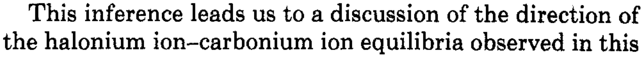
Scheme III



Having accounted for the formation of trimethylated ion **12** in terms of the less favored opening of the six-membered-ring **10h** at the primary position (Scheme III), it remains for us to note that rearrangement of the tertiary ion **10c**, present in large amount, accounts for the formation of the methylethyl species **11h** $\rightleftarrows$ **11c.** A similar rearrangement occurs in the *tert*-amyl cations, resulting in carbon scrambling.[7] Our results do not show whether **10** and **11** are present in a thermodynamically controlled equilibrium or whether they are formed in the observed proportions in a kinetically controlled process during the initial reaction of halide precursors.

Completing our survey of the status of primary, secondary, and tertiary six-membered-ring chloronium ions, we note that presently unknown secondary chloronium ions such as **16h** (Scheme IV) should be in rapid equilibrium with small amounts of the corresponding secondary carbonium ions. This conclusion is implied by the observation that hydrogen scrambling broadens the hydrogen multiplet of the CH_3 group of ethylated ion **19h** at −65°.[3] Since the six-membered ring is a minor component in the mixture, we infer that monoalkylated five-membered-ring **17h** is more stable than the comparable six-membered-ring **16h.**

Scheme IV



This inference leads us to a discussion of the direction of the halonium ion–carbonium ion equilibria observed in this study and the earlier one. The most noteworthy result is that the six-membered-ring **10h** is predominantly opened to **10c**, whereas five-membered rings have all been present predominantly in the closed form. Although molecular orbital energy levels may play a part in these ring size effects (cf. ref 4), the observed effect may actually be due to a mixture of enthalpy and entropy effects which should be considered in detail. In principle, both enthalpy and entropy differences for the equilibria may be determined from the data in Table III. However, the values so determined may not be accurate enough for meaningful comparison. It is apparent, however, that the closed species is favored by enthalpy for both the five-membered-ring ions and the six-membered-ring ion, since the open-chain species increases in concentration with higher temperature for all cases and $d(\ln K)/d(1/T) = -\Delta H/R$. Therefore, at least for **10** the entropy difference is the overriding factor in determining to which side the equilibrium lies. For hydrocarbons equilibria between open and closed species have been found to favor the closed species more highly when a five-membered ring rather than a six-membered ring is involved.[8] Comparable effects could account for part or all of the preference for five-membered-ring formation observed in our study. However, still another effect remains to be considered. The carbonium ions in equilibrium with five-membered rings are probably destabilized relative to those derived from six-membered rings because the electronegative halogen substituents of the former are closer (by one methylene group) to the positive charge. If the magnitude of the effect is comparable to that in transition states for solvolyses, the available data suggest that a threefold effect on the ratio of *K* values might be expected from this factor alone.[9]

Conclusion

The value of ^{13}C NMR in the analysis of equilibria involving a complex mixture of equilibrating ions is illustrated by the present study. Since there are very few systems in which equilibrium constants can be determined in ring-forming reactions, the system described here presents a rare opportunity to assess factors governing the energetics of formation of five- and six-membered rings.

Experimental Section

The ^{1}H NMR spectra were obtained on Varian A-60 and XL-100-15 instruments. Chemical shifts were referenced to a capillary of Me_4Si in SO_2 or internal Me_4Si in carbon tetrachloride. The ^{13}C NMR spectra were obtained by the Fourier transform method on the Varian XL-100-15 with noise decoupling and between 500 and 1000 pulses. Chemical shifts were measured from CF_2BrCF_2Br in a 5-mm tube within the 12-mm tube and were corrected to capillary Me_4Si using a value of 115.32 ppm for the difference in chemical shifts between Me_4Si and $(CF_2Br)_2$. Temperature measurements were made as previously described.[3]

Ionic Solutions. The ion solutions were made in 5-mm NMR tubes by addition of 0.27 mmol of one of the dichlorides to 0.5 ml of a 1.25 *M* solution of SbF_5 (Ozark Mahoning, redistilled) in SO_2 (0.68 mmol of SbF_5). The solutions were cooled in a dry ice–acetone bath during the addition with stirring with a Nichrome wire. Similar proportions were used in the preparation of samples in 12-mm tubes for ^{13}C spectroscopy. Some NMR samples were also taken from solutions prepared in a volumetric flask for reaction with methanol (see below).

1,7-Dichloroheptane was prepared by reaction of 18.51 g of 1,7-heptanediol (0.14 mol) with 36.64 g of thionyl chloride (0.31 mol) in 25.31 g of pyridine (0.32 mol). The product was separated after extraction by spinning-band distillation, bp 95–97° (13 mm).

Anal. Calcd for $C_7H_{14}Cl_2$: C, 49.72; H, 8.34. Found: C, 49.66; H, 8.43.

1,4-Dichloro-4-methylhexane. To a solution of 24.51 g (0.20 mol, Aldrich) of γ-chlorobutyric acid in 150 ml of dry ether in a dry, nitrogen-flushed flask was added dropwise 278 ml (0.50 mol, Lithcoa) of methyllithium solution. Total addition time was 1.5 hr, after which 60 ml of water was added dropwise with cooling in ice. The ether solution was washed twice with water and dried over Na_2SO_4. Spinning-band distillation gave 13.2 g (55%) of 5-chloro-2-pentanone, bp 73–75° (22 mm).

In a 500-ml, dry, nitrogen-flushed flask were placed 2.67 g (0.11 mol, MCB for Grignard) of magnesium turnings and 50 ml of dry ether. A solution of 11.99 g (0.11 mol) of ethyl bromide in 50 ml of ether was added dropwise with cooling in ice. The solution was allowed to warm to room temperature and then was stirred for 0.5 hr after which 12.06 g (0.10 mol) of the 5-chloro-2-pentanone was added with cooling. After the solution had returned to room temperature, 15 ml of a saturated solution of ammonium chloride was added to precipitate the magnesium salts. The ether solution was filtered, and solvent was removed by distillation. The remaining liquid was stirred with concentrated HCl for 20 min, then was extracted into CH_2Cl_2. The CH_2Cl_2 solution was washed once with 7 *N* sulfuric acid, once with saturated $NaHCO_3$ solution, and with water. Spinning-band distillation resulted in 8.9 g of product boiling at 68–69° (6 mm) (58% yield from the ketone), ^{1}H NMR (CCl_4) δ 3.50 m, 2 H; 1.5–2.0 m, 6 H; 0.98 t, 3 H.

Anal. Calcd for $C_7H_{14}Cl_2$: C, 49.72; H, 8.34. Found: C, 49.73; H, 8.34.

1,5-Dibromo-5-methylhexane. Hydrogen bromide was bubbled through a solution of 35.01 g (0.35 mol, Aldrich) of δ-valerolactone in 500 ml of anhydrous ethanol for 3 hr. The solution was poured into 250 ml of water which was then extracted five times with CH_2Cl_2. The organic solution was dried with Na_2SO_4 and distilled to give 23.4 g of ethyl 5-bromopentanoate: bp 63° (0.4 mm); yield 32%; ^{1}H NMR δ 4.05 t, 3.35 t, 2.24 m, 1.80 m, 1.22 t.

A Grignard reaction was carried out using 20.7 g (0.1 mol) of ethyl 5-bromopentanoate, 31.2 g (0.22 mol) of methyl iodide, and 5.35 g (0.22 mol) of magnesium. The procedure was the same as that used above for 1,4-dichloro-4-methylhexane. The liquid remaining after removal of the ether was allowed to react with 100 ml of concentrated hydrobromic acid for 20 min. The product was extracted into CH_2Cl_2 which was then washed with saturated $NaHCO_3$ solution and a saturated solution of $Na_2S_2O_3$. Attempted distillation on a spinning-band column gave a material having olefinic peaks in the ^{1}H NMR spectrum. The remaining material was extracted with concentrated sulfuric acid, then with sodium bicarbonate solution, then water. A short-path distillation (90°, 0.2 mm) led to 1.55 g of clear liquid: ^{1}H NMR δ 1.72 s, 3.35 t.

Anal. Calcd for $C_7H_{14}Br_2$: C, 32.59; H, 5.47. Found: C, 32.71; H, 5.35.

1,5-Dichloro-5-methylhexane was prepared from δ-valerolactone (35.0 g) by the same procedure used for 1,5-dibromo-5-methylhexane except that ring opening was accomplished with hydrogen chloride gas.

Distillation gave ethyl 5-chloropentanoate, 26.1 g (46%), bp 85–90° (12 mm). A portion of the ester (24.6 g) was allowed to react with methylmagnesium iodide to give an ether extract which was allowed to react with 100 ml of 12 *M* HCl for 1 hr. Distillation of the ether extract gave 16 g, bp 30–63° (2 mm), in five fractions, shown by NMR to contain an impurity thought to be 1-iodo-5-chloro-5-methylhexane: ^{1}H NMR δ 1.55 s, 1.70, 3.50 t.

Anal. Calcd for $C_7H_{14}Cl_2$: C, 49.72; H, 8.35. Found: C, 49.72; H, 8.34.

Reaction of Ions with Methanol. Ionic solutions prepared from 1,7-dichloroheptane and 1,5-dichloro-5-methylhexane were allowed to react with methanol, and the products were collected by distillation. The procedure for the solution prepared from 1,5-dichloro-5-methylhexane is described in detail. The 1,5-dichloro-5-methylhexane (12.50 g, 0.07 mol) was dissolved in 40 ml of sulfur dioxide. This solution was added to a mixture of 40.07 g of SbF_5 (0.18 mol) and 50 ml of sulfur dioxide with agitation. The ^{1}H NMR and the ^{13}C NMR spectra of the resulting solution indicated that there were roughly equal concentrations of the three ions **10, 11,** and **12.** (The solution from 1,7-dichloroheptane contained a larger relative concentration of **12,** possibly owing to heating by the reaction.)

The SO_2 solution was poured into 100 ml of methanol containing 10 g of K_2CO_3. The temperature was maintained below 40°. The solution was allowed to evaporate at room temperature and was poured into 100 ml of H_2O and 100 ml of CH_2Cl_2. A yellow precipitate was removed by filtration, and the CH_2Cl_2 solution was washed with saturated $NaHCO_3$ and H_2O. An emulsion formed which was partially broken by addition of saturated NaCl. Removal of solvent and spinning band distillation gave 15 fractions (Table IV).

Table IV

Fraction	Temp, °C	Pressure, mm	Weight, g
1	42–49	13	0.37
2–5	49–59	13	0.82
6–11	61–68	13	3.16
12–14	70–72	13	0.94
15	60	1.5	0.80

^{1}H NMR spectra of the undistilled material and fractions 2, 5, 6, 7, 10, 13, 14, and 15 were recorded. All of the fractions were also analyzed by VPC (DC 550, 163°, glass column). Unfortunately, variable results indicated that some elimination occurred during VPC analysis even with the glass column. Furthermore, while there was no large olefinic peak in the ^{1}H NMR spectrum of the undistilled material, the spectra of fractions 2 and 5 had substantial intensity between δ 4.9 and 5.1 indicating that some elimination also occurred during distillation.

The NMR spectra of fractions 5, 6, and 7 showed that 2-chloro-5-methoxy-5-methylhexane (**15**), derived from 1,1,4-trimethyltetramethylenechloronium ion, was the major component, but some olefin was also present. The ^{1}H NMR spectrum of fraction 10 had much smaller olefinic peaks, and the ^{13}C NMR spectrum and the VPC analysis matched that of authentic **15.**

The ^{1}H and ^{13}C NMR spectra of fraction 15 indicated that it was a mixture of chloro ethers **13** and **14,** whose spectra were available from reference samples described below. Fractions 13 and 14 were mixtures of **13, 14,** and **15** and also contained olefin. The ethers **13** and **14** are the expected products of reaction of 1,1-dimethylpentamethylenechloronium ion and 1-methyl-1-ethyltetramethylenechloronium ion, respectively.

Solutions of chloro ethers **13**, **14**, and **15** were prepared by solvolysis of 0.005 mol of the corresponding dichlorides in 5 ml of methanol containing 1.0 g of $NaHCO_3$. The reactions were followed by VPC (DC 550, 163°, glass column) and required about 9 hr reflux for completion. The products were isolated in 5 ml of CCl_4 which was washed twice with 5-ml portions of water. The ^1H NMR spectra of the products indicated that some elimination occurred during solvolysis. Nevertheless, only very minor peaks in the ^{13}C NMR spectra of the undistilled products could not be assigned to the desired substitution products, except for the solvolysis which yielded **14**. In this instance, olefin was removed by distillation at ~1 mm pressure before the NMR spectra of the undistilled residue were obtained.

The ^{13}C NMR spectrum of **13** was recorded at room temperature in CCl_4. Chemical shifts relative to the solvent peak were converted to Me_4Si reference by subtraction of 96.0 ppm. The chemical shifts (parts per million from Me_4Si) follow: 73.5, *t*-C; 48.6, OCH_3; 44.1, $-CH_2Cl$; 39.6, $-CH_2-$; 33.1, $-CH_2-$; 24.8, $-CH_3$; 21.1, $-CH_2-$.

The ^{13}C NMR chemical shifts of **14** follow: 45.0, $-CH_2Cl$; 34.4, $-CH_2-$; 30.0, $-CH_2-$; 26.7, $-CH_2-$; 22.0, $-CH_3$; 17.9, $-CH_3$. (The methoxy peak was weak in all of the spectra, probably owing to a long relaxation time, and was not always observed with certainty.)

The ^{13}C NMR chemical shifts of **15** follow: *t*-C, 58.3, C-Cl; 37.0, $-CH_2-$; 34.3, $-CH_2-$; 25.5, 25.1, and 24.8, $-CH_3$. (Note that the three methyl groups are nonequivalent owing to the asymmetric carbon.)

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Registry No.—**7**, 821-76-1; **8**, 54305-92-9; **9**, 54305-94-1; **10c**, 57256-52-7; **10h**, 57256-53-8; **11c**, 57256-54-9; **11h**, 57256-55-0; **12c**, 57256-56-1; **12h**, 50635-30-8; **13**, 57256-57-2; **14**, 57256-58-3; **15**, 57256-59-4; 1,7-heptanediol, 629-30-1; γ-chlorobutyric acid, 627-00-9; 5-chloro-2-pentanone, 5891-21-4; 1,5-dibromo-5-methylhexane, 54305-93-0; δ-valerolactone, 542-28-9; ethyl 5-bromopentanoate, 14660-52-7; ethyl 5-chloropentanoate, 2323-81-1.

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Notes

The Rapid HI Cleavage of Ethers and Ketals in Acetonitrile. Catalysis by CH_3OCHI_2 and Preparation of Formates

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The use of ethers as alcohol protecting groups in synthesis has aroused recent interest.[1] Ganem noted "the dearth of gentle yet effective techniques for releasing the parent alcohol". We wish to report that the use of acetonitrile as solvent with diiodomethyl methyl ether (DIME) catalysis promotes the classic HI cleavage[2] into the gentle and effective category at least for primary and secondary alkyl methyl ethers. Methyl ethers may be cleaved in good yield in 30 min or less at room temperature (Table I). At the cost of increasing the reaction time to hours, cleavage may be accomplished with 1 equiv of HI generated in controlled fashion by the addition of toluenesulfonic acid hydrate to excess sodium iodide. Other gentle and selective reagents are available for ether cleavage.[3,4]

The HI cleavage of ethers in acetonitrile exhibits all the hallmarks of the classic reaction.[2]

$$ROCH_3 + HI \rightleftarrows ROH(CH_3)^+ \begin{cases} \nearrow ROH + CH_3I \\ \searrow R^+ \longrightarrow RI \end{cases}$$

When R is primary or simple secondary alkyl group, the methyl–oxygen bond is cleaved. When R^+ is a good carbonium ion, such as tertiary alkyl or benzyl, iodide is the predominant product. *exo*-Norbornyl shows intermediate behavior, yielding a 50:50 mixture of iodide:alcohol. Chiral 2-octyl methyl ether is cleaved with complete retention of the C-2–O bond. Ethers which are strong Lewis bases, such as tetrahydrofuran, 7-oxanorbornane, epoxides, and, of synthetic importance, ketals, are all cleaved readily. Cyclohexanone and camphor are regenerated in excellent yield from their ethylene glycol ketals in 5 min at room temperature in the presence or absence of DIME. Ethers which are weak Lewis bases such as tetrahydropyran, dibutyl ether, and anisole are unaffected at room temperature.[5]

DIME, prepared in situ from 1,1-dichloromethyl ether (DCME) and sodium iodide, catalyzes ether cleavage and yields formate as the predominant product. Initial speculation suggested that the oxonium ion CH_3OCHI^+ acted as a Lewis acid catalyst for the cleavage in the same manner as the reported catalysis by acetyl derivatives.[6] However, unyielding experiments showed that if all reagents are rigor-