N',N'-Diacetyl-N-aminocamphorimide (IIIj) was obtained by refluxing N-aminocamphorimide (IIIa) with acetic anhydride for about 2 hr, the excess of the latter being removed off under reduced pressure and the product being recrystallized from ethanol, mp 115°.

Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 60.00; H, 7.14. Found: C, 59.73; H, 7.49.

N',N'-Dibenzyl-N-aminocamphorimide (IIIl) was obtained by heating N-aminocamphorimide with 2 mol of benzyl chloride in the presence of pyridine at 120° for about 2 hr. The excess of benzyl chloride and pyridine were removed off under reduced pressure and the product was recrystallized from ethanol, mp 152°.

Anal. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.59; H, 7.44. Found: C, 76.81; H, 7.62.

N,N'-Biscamphorimidyl (IIIm) was obtained by heating a mixture of 2 mol of camphoric anhydride and 1 mol of hydrazine hydrate at 240–250° for 3–4 hr. It was recrystallized from hot ethanol, mp 350°.

Anal. Calcd for $C_{20}H_{28}N_2O_4$: C, 66.66; H, 7.77; mol. wt, 360. Found: C, 66.27; H, 7.83; mol wt, 362. The molecular weight of the sample was determined by an osmometer (Mechrolab Model 301 A).

The nmr spectra were recorded on a Varian A-60D spectrometer equipped with a variable-temperature controller Model V-6040. Ir spectra were recorded in Nujol on Perkin-Elmer spectrophotometers (Model 621 and 257). Ir and nmr data (excluding chemical shifts of the methyl groups listed in Table I) and the melting points are recorded in Table II.

Registry No.—IIIa, 37710-30-8; IIIb, 37710-31-9; IIIc, 37710-32-0; IIId, 37710-33-1; IIIe, 37710-34-2; IIIf, 37710-35-3; IIIg, 37710-36-4; IIIh, 37710-37-5; IIIi, 37780-36-2; IIIj, 37710-38-6; IIIk, 37710-40-0; IIIl, 37710-39-7; IIIm, 37710-41-1; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4; m-toluoyl chloride, 1711-06-4; ethyl chloroformate, 541-41-3; propionyl chloride, 79-03-8; trifluoroacetyl chloride, 354-32-5; acetic anhydride, 108-24-7; benzyl chloride, 100-44-7; camphoric anhydride, 76-32-4.

Acknowledgment.—Thanks are due to Professor G. B. Singh for his keen interest and to Professor N. V. Riggs, University of New England, Australia, for recording a variable-temperature spectra of the compound IIIj.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Tetramethylenehalonium Ions

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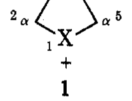
Received August 16, 1972

Carbon-13 nmr chemical shifts for the cyclic five-membered halonium ions and their precursors have been tabulated. Consistent downfield shifts of 30–35 ppm have been observed for the halo-substituted carbon (α carbon) in going from precursor to ion when the α carbon is primary. Addition of a methyl group to the α carbon of a substituted ion causes a 35-ppm downfield shift. The coupling constants for these ions have also been tabulated. A 10–15-Hz increase in the J values of the α carbons of halonium ions, compared to J values for precursors, was observed. These data suggest that highly electronegative heteroatoms give carbonium ion character to the attached carbons.

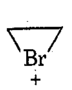
Since the preparation of the stable five-membered tetramethylenehalonium ions[2] **1** their reactions with various nucleophiles have been studied.[3] In the case of the tetramethylenechloronium ion, rate studies[4] with various carboxylic acids in SO_2 at −65° gave rate constants which were significant as possible measures of the nucleophilicities of the carboxylic acids.



1

We have recently prepared halonuum ions with alkyl or halo substituents at the 3 position of the ring and have studied the direction of ring opening by a variety of nucleophiles. The relative percentages of products formed appeared to be affected by the inductive and steric effect of the ring substituent and the nucleophilicity of the nucleophile.[5]

Olah and White have correlated the charge density on various carbons of positively charged species with the ^{13}C chemical shift.[6a] Among the species investigated were the ethylenebromonium (**2**) and tetramethylethylenebromonium (**3**) ions. Reported chemical shifts of the ring carbons were 120.8 and 55.2 ppm, respectively, upfield from CS_2.[6a,7] It was shown that ^{13}C chemical shifts offer a possibility of distinguishing open chain, equilibrating, and bridged cationic species.[6]



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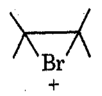
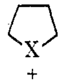
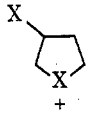


3

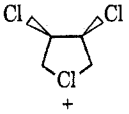
We now wish to report ^{13}C nmr data (δ_{CS_2} and J_{CH}) for the five-membered halonium ions **4**–**13** and their precursors (Table I). Our study provides an illustration of the applicability of presently available instru-



4, X = Cl
5, X = Br
6, X = I



7, X = Cl
8, X = Br



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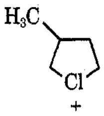

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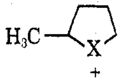

11, X = Cl
12, X = Br
13, X = I

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[1] Postdoctoral Investigator.

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

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

[4] P. E. Peterson and F. J. Waller, *ibid.*, **94**, 991 (1972).

[5] P. E. Peterson and B. R. Bonazza, *ibid.*, **94**, 5017 (1972).

[6] (a) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969), and references cited therein; (b) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

[7] G. A. Olah and R. D. Porter, *ibid.*, **93**, 6877 (1971).

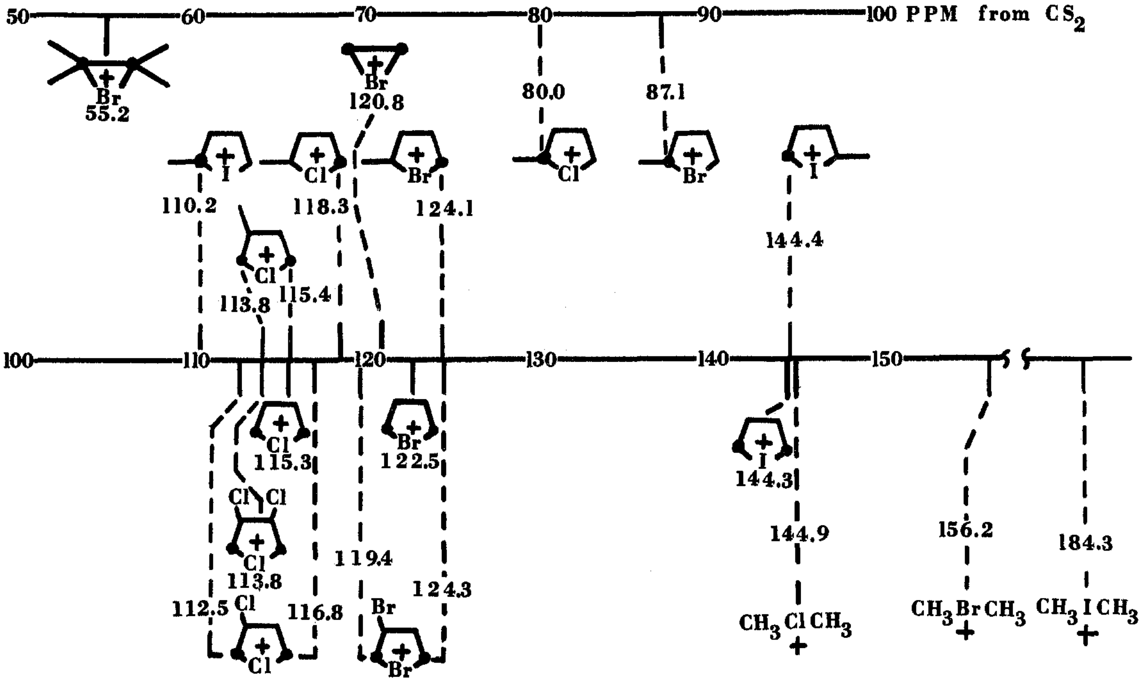

Figure 1.—Carbon-13 chemical shifts of the tetramethylenehalonium ion α carbons relative to 0.8 M CS_2 in SO_2 at $-65°$. Also plotted are Olah's values for the dimethylhalonium, the ethylenebromonium, and the tetramethylethylenebromonium ions.

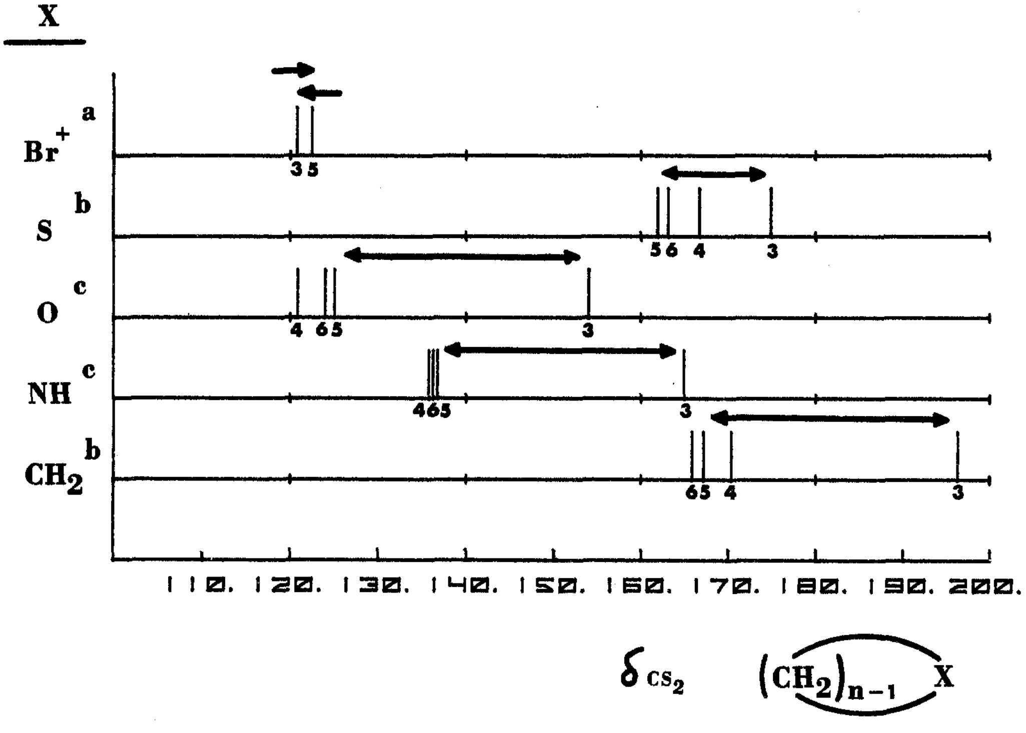

Figure 2.—Carbon-13 chemical shifts of heterocycles and cycloalkanes. For heteroycles the δ value for the heterosubstituted (α) carbon is plotted for the ring size indicated by the number. Arrows indicate the differences in chemical shifts between three- and five-membered rings. (a) Reference 6A and this work. (b) Values obtained in our laboratories. See Experimental Section for values. (c) Reference 12a.

mentation to practical organic problems.[8] The combination of large nmr sample tubes (12-mm spinning) and pulsed Fourier transform mode of operation allowed us to obtain both noise decoupled and coupled spectra from 0.6–0.8 M solutions in 12-mm tubes. Previously, coupling information for ions in SO_2 has been obtained from INDOR experiments in which side bands in the hydrogen spectra arising from coupling to ^{13}C are utilized. Owing to overlapping of hydrogen resonances, many of the results reported here possibly could not have been obtained by the INDOR method.

Chemical Shifts.—A plot of the chemical shifts relative to CS_2 is shown in Figure 1 and further comparisons are given in the plot of Figure 2, to be discussed later. By the use of 3000–5000-Hz sweep widths and centered 5-mm 1,2-dibromo-1,1,2,2-tetrafluoroethane ($C_2F_4Br_2$) lock capillaries the decoupled spectra shown in Figures 3 and 4 could be obtained in

[8] See Experimental Section for description of instrumentation.

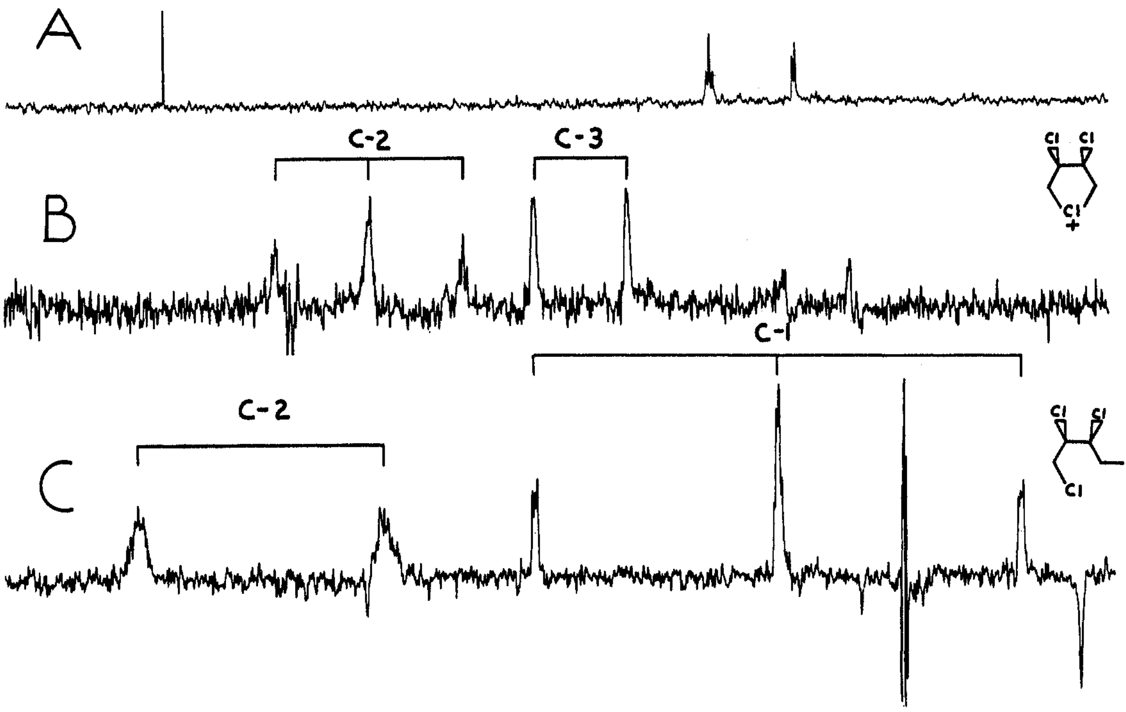

Figure 3.—(A) Off resonance decoupled ^{13}C spectrum of 0.6 *M* **9** in SO_2 at −65°; 5000-Hz sweep width; 238 pulses. (B) Coupled ^{13}C spectrum of 0.6 *M* **9** in SO_2 at −65°; 2000-Hz sweep width; 5400 pulses. (C) Coupled ^{13}C spectrum of 1.5 *M* precursor to ion **9** in CCl_4 at 25°; 700-Hz sweep width; 1300 pulses.

TABLE I

^{13}C NMR DATA FOR THE TETRAMETHYLENEHALONIUM IONS

Ion	C-2		C-3		C-4[c]		C-5[c]		CH_3–	
	δ_{CS_2}[a]	J_{CH}[b]	δ_{CS_2}	J_{CH}	δ_{CS_2}	J_{CH}	δ_{CS_2}	J_{CH}	δ_{CS_2}	J_{CH}
4					159.2	137	115.3	165		
					(4.1)	(7)	(31.8)	(14)		
5					157.2	136	122.5	165		
					(4.8)	(7)	(35.0)	(11)		
6					155.0	135	144.3	160		
					(4.3)	(7)	(39.3)	(10)		
7	112.5	167	131.8	164	151.3	140	116.8	167		
	(31.1)	(13)	(1.9)	(12)	(4.6)	(10)	(33.5)	(14)		
8	119.4	167	141.4	166	148.9	138	124.3	168		
	(35.6)	(9)	(−0.9)	(9)	(5.7)	(9)	(35.3)	(13)		
9					128.9	168	113.8	170		
					(4.3)	(12)	(31.5)	(16)		
10	113.8		150.8		153.2		115.4		178.7	
	(27.4)		(9.8)		(4.0)		(33.5)		(−2.6)	
11[d]	80.0		152.2		158.2		118.3		171.1	
12[d]	87.1	165	149.5	135	156.9	137	124.1	165	170.1	132
	(51.0)	(15)	(4.2)	(5)	(5.1)	(8)	(33.0)	(13)	(−3.7)	(3)
13[d,e]	110.2	159	146.0	132	155.4	129	144.4	157	168.9	132

[a] Referenced to 0.8 *M* CS_2 in SO_2 at −55° by adding 78.1 to $\delta_{CF_2BrCF_2Br}$. To reference shifts to pure CS_2 at −65° add 0.5 ppm. To reference shifts to capillary CS_2 −65° add 1.6 ppm. Values in parentheses are $\Delta\delta$ precursor ion. [b] Values in parentheses are ΔJ ion precursor. [c] For symmetrical ions C-4 and C-5 are equivalent to C-3 and C-2, respectively. [d] Assignment of C-3 and C-4 may be reversed. [e] We are indebted to Dr. P. M. Henrichs for the data on ion **13**.

1.5–3 min (200–400 pulses). We referenced our chemical shifts to the easily recognized center peak of the triplet of triplets given by the $C_2F_4Br_2$ lock material (J_{CF} = 313 Hz, J_{CCF} = 39 Hz) contained in an inner concentric tube. The $C_2F_4Br_2$ capillary signal was separately shown to be 78.1 ppm upfield from CS_2 in SO_2 at −55°. Direct use of CS_2 as a reference was inconvenient because its weak intensity was easily confused with frequently encountered spurious singlets.[9]

As seen in Figure 1, the chemical shifts of the primary α carbons of the five-membered ions **1** tend to fall in regions which are characteristic of the halogen. The characteristic regions are 112–119 (X = Cl), 119–125 (X = Br), and 144–145 ppm (X = I). Chemical shifts for the halo-substituted carbon atoms of ions are 30–35 ppm downfield from those for dihalide precursors (*cf.* Table I).

Substitution of a methyl group for hydrogen at C-2 in the five-membered halonium ion ring (ions **11**, **12**, and **13**) causes an unusually large downfield shift (~35 ppm) of C-2 relative to the shift of C-2 in the unsub-

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[9] Singlets may be introduced by the computer or may be "foldovers." See Thomas C. Farrar and Edwin D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971.

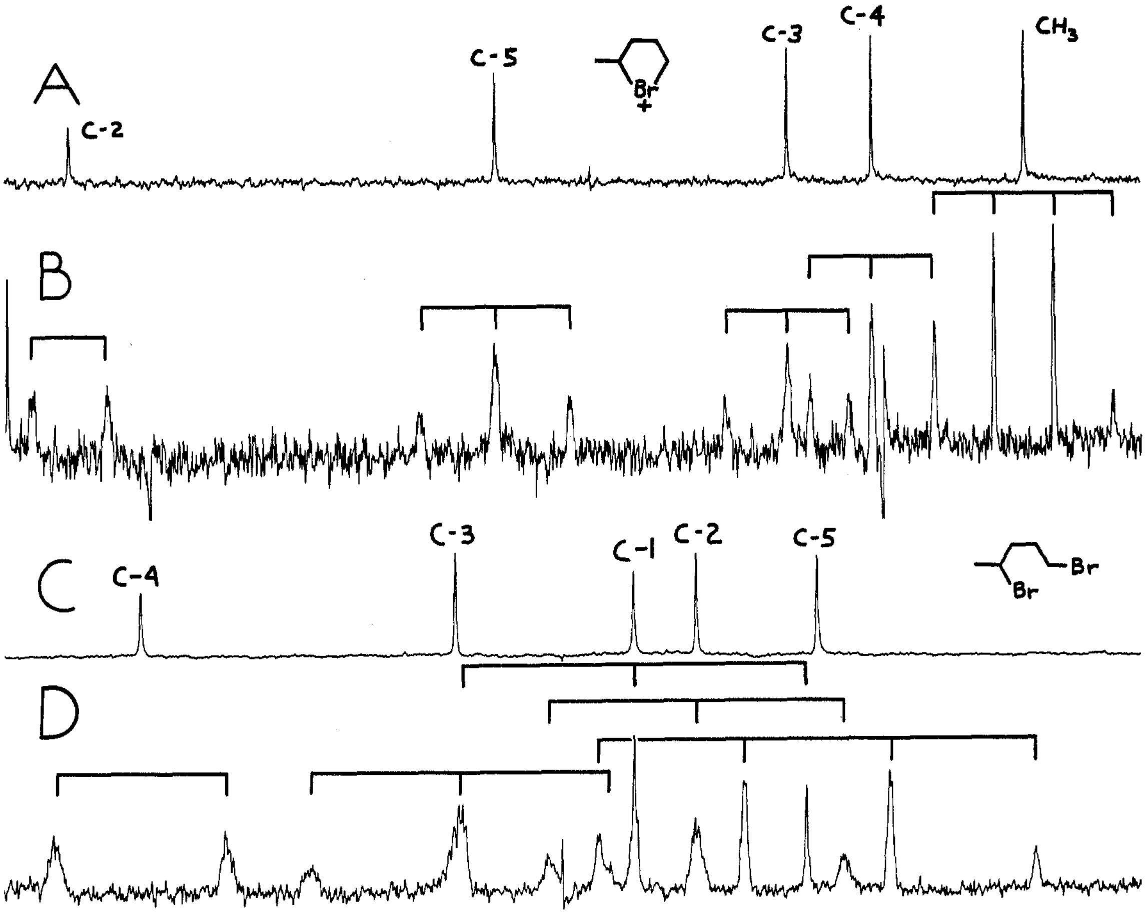

Figure 4.—(A) Noise decoupled (300 pulses) and (B) coupled (5200 pulses) ^{13}C spectra of 0.6 *M* **12** in SO_2 at −65°; both at 2500-Hz sweep widths and identical offsets. (C) Noise decoupled (22 pulses) and (D) coupled (150 pulses) ^{13}C spectra of the precursor to ion **12** neat at 25°.

stituted ions **4**, **5**, and **6**. We shall discuss this effect later. In contrast to the downfield shift of C-2 in methyl-substituted ions **11** and **12**, the primary carbon at C-5 tends to shift upfield slightly relative to the unsubstituted ions **4** and **5** (Figure 1). Substitution of chlorine at C-3 in ion **4** (giving **7**) tends to cause a downfield shift of C-2 with smaller upfield shift at C-5. When an alkyl group is substituted at C-3 (ion **10**) the shifts at C-2 and C-5 are seen to be much smaller but in the same direction as for 3-chlorosubstituted ion **7**. Similar shifts can be seen for halo-substituted ions **8** and **9** (Figure 1).

Dependence of the ^{13}C chemical shift on concentration for ion **4** and its precursor was determined in SO_2 at −65°. The effect of concentration over the range from 0.17 to 0.6 *M* was found to be negligible for both. Also the dependence of the chemical shift of ion **4** on excess SbF_5 was found to be negligible when solutions containing 0.16 *M* **4** prepared from 2:1 and 4:1 molar ratios of SbF_5 to 1,4-dichlorobutane were compared.

Although there does not appear to be any temperature dependence of $\delta_{C_2F_4Br_2}$ for the ion **4** over the range from −65 to −25°, there does seem to be a small dependence for the primary carbons in the precursor, 1,4-dichlorobutane. When $\delta_{C_2F_4Br_2}$ for the primary carbons in 1,4-dichlorobutane was plotted *vs.* temperature a straight line was obtained with a slope of 0.016 ppm/°C corresponding to a small downfield shift with decreasing temperature. A similar dependence of 0.031 ppm/°C was noted for the primary carbons of 1,4-diiodobutane (precursor to ion **6**). The temperature dependence of the spectra of precursors is probably due to conformational changes (C–C rotation) which are not possible for the ion. However, the lock material is in principle subject to temperature effects of conformational origin which would lead to modification of the above discussion.

Coupling Constants.—Owing to the absence of Overhauser enhancement and because of the greater multiplicity of the peaks, determination of coupled spectra (on 0.6–0.8 *M* solutions) required from 30 to 75 min (2000 to 5000 pulses). Coupled spectra for ions **9** and **12** are shown in Figures 3 and 4.

The fluorine lock material used to obtain coupled spectra was trichlorofluoromethane (CCl_3F), chosen because its carbon atom appears to have a long relaxation time, and, thus, its absorption is not seen in the coupled spectrum either directly or as a foldover.[9] The use of 1000–2000-Hz sweep widths was necessary to obtain coupling constants to the accuracy at ±2 Hz measured directly from the spectrum. Unresolved longer range ^{13}C–H coupling and concomitant dependence of the peak midpoint upon the phase control settings limit the accuracy of measurement.

Table I shows that J_{CH} values for C-2 and C-5 in the five-membered halonium ions range from 160 to 170 Hz, whereas the methylene carbons β to positive halogen (C-3 and C-4) have lower values, 130–140 Hz. This difference in J_{CH} between the two types of carbon atoms aided in the assignment of their resonances when peak multiplicities were the same. The coupling constants for the C-2 and C-5 carbons in the five-membered ions are of the same magnitude as those obtained by Olah and DeMember for the dimethylhalonium ions.[10] The larger coupling constant observed for the ethylenebromonium ion (J_{CH} = 185 Hz) has been attributed to the effect of the three-membered ring.[6a]

Discussion

The factors which affect ^{13}C chemical shifts and coupling constants are not fully understood.[11] However, we shall discuss our results based on available empirical generalizations as follows, despite the well-recognized limitations of the approach. (1) Downfield shifts and increased J ^{13}C–H coupling constants occur as the charge on ^{13}C becomes more positive. (2) Downfield shifts and increased J ^{13}C–H coupling constants occur as the hybridization on carbon changes from p to sp^3 to sp^2 to sp. Whether electronegative substituents exert their effect directly or by changing the hybridization on carbon (with interorbital angles not equal to bond angles) is debatable.[11] (3) An effect is present which leads to upfield ^{13}C shifts as the atomic number of the element attached to carbon increases in a column of the periodic table. For example, δ ^{13}C for C–I is upfield from that for C–H, that of C–Br is near to that of C–H, and that of C–Cl is downfield from that of C–H.

Carbon-13 chemical shifts for five-membered ring bromonium ions are best interpreted by comparison with values of chemical shifts of cyclic alkanes, amines, ethers, and sulfides, along with the available[6a] value for the three-membered ethylenebromonium ion. When the shifts for carbon attached to the heteroatom in these compounds[12] are plotted, the values for the five-membered rings, compared to those for the three-membered rings, form a suggestive pattern, illustrated in Figure 2, where arrows connect δ values for the two ring sizes. As has been noted,[12a] for cyclopropane, ethylenimine, and ethylene oxide the carbons of the three-membered ring are strikingly more shielded than those for other ring sizes. For ethylene sulfide the chemical shift of the three-membered ring is closer to that of the other rings, whereas for the cyclic bromonium ions, the carbons of the three-membered ring are less shielded than those of the five-membered ring, whose δ value is reported in the present paper. The number of five-membered ring halonium ions which we have measured is large enough to assure that the range of δ values is small for primary carbons of this ring size and that the patterns of Figure 1 are not substantially influenced by unpredictable variations in δ. Even the presence of electronegative substituents on the carbon atom β to the positive halogen in ions **7**, **8**, and **9** results in only a slight deshielding effect (2–3 ppm) at the α carbon. This result is not surprising, since "β effects" for substituents at this distance from the carbon under examination have been found in aliphatic systems to be moderate in size (~6 ppm) and not markedly dependent on the electronegativity of the substituent.[13] The chemical shift effects of Figure 2 would be observed if the carbon atoms of the three-membered ring bromonium ion, and to a lesser extent of the corresponding sulfide, are unusually positive and/or if the geometry of the CH_2CH_2 system is displaced toward planarity corresponding to a hybridization more like that of ethylene. These observations suggest the possibility that the unfilled d orbitals of bromine and sulfur accept electrons from the filled molecular orbitals of the ring. This would give the ring carbon atoms a net positive charge and cause the downfield shifts observed. The positive bromine, although from a higher row in the periodic table, is presumed to be a better acceptor than uncharged sulfur because of the influence of the positive charge.

In a separate publication one of us has examined the possibility of transfer of charge from Walsh type ring orbitals to d orbitals. Based on the symmetry properties of the ring orbitals and the d orbitals, charge transfer may be favored in odd-sized rings,[14] although other properties of the orbitals could negate this postulate. Based on overlap considerations, the small rings are predicted to exhibit the postulated stabilization of odd-sized rings to the greatest extent. Accordingly, the three-membered ring bromonium ion chemical shift can be considered to reflect the substantial shielding exhibited by three-membered rings, in combination with a larger deshielding effect resulting from charge transfer to bromine to give the observed chemical shift 35 ppm downfield from the 1,2-dibromoethane. Based on a 30-ppm shielding effect ($\Delta\delta$, cyclohexane to cyclopropane), the deshielding effect resulting from charge transfer would be approximately 65 ppm. If the large heteroatom blocks some of the shielding effect in the three-membered ring, as has been hypothesized,[12] the estimates given here would be modified.

In the case of the five-membered ring halonium ions the 35-ppm downfield shift caused by introduction of a 2-methyl substituent is suggestive of charge transfer from the ring carbon orbitals to halogen. The methyl group may be postulated to promote increased carbonium ion character at the halo-substituted carbon, since the methyl substituent effect is much greater than that found for hydrocarbons (~8 ppm)[15] and other compounds.[16] The presently available data do not suggest whether the charge transfer from carbon arises from filling of d orbitals, mentioned above, or merely from σ-bond polarization, however. In any event, the 35-ppm effect may be compared with the approximate 290-ppm change in ^{13}C chemical shift attendant upon converting a hydrocarbon to a carbonium ion, to yield an estimate of $^{35}/_{290}$ or 12% increase in cationic character at the halo-substituted carbon upon methyl substitution.

Although the above discussion has been developed largely as a correlation of chemical shifts, it is to be noted that other evidence from the literature is con-

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[10] G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 718 (1970).

[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 988.

[12] (a) G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965). (b) We have remeasured some of the values, as indicated in the footnotes of Figure 2 and as described in the Experimental Section.

[13] (a) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971); (b) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).

[14] P. E. Peterson, *J. Org. Chem.*, **37**, 4180 (1972).

[15] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

[16] T. F. Page, Jr., T. Alger, and D. M. Grant, *ibid.*, **87**, 5333 (1965).

sistent with the ring size effects and alkyl substituent effects which we discussed. Rerrangement reactions studied in Olah's group showed a strong preference for three- and five-membered ring halonium ion formation.[17] Larsen and Metzner[18] found 8–19 kcal/mol of stabilization in three-membered ring bromonium ions. These authors also found increased sensitivity to methyl stabilization in the three-membered ring, compared to five, indicative of the carbonium ion nature of carbons in the three-membered ring. Our work shows that ^{13}C nmr effects in five-membered rings are well accommodated within a framework which correlates the properties of the halonium ions and other cyclic compounds as a function of structure and ring size.

Experimental Section

Chemicals.—All dihalide precursors to the various ions were either commercially available materials or prepared as described previously.[5] The cyclic sulfides and alkanes whose nmr line positions are listed in Figure 2 also were commercially available.

Preparation of the Ions.—The ions were prepared at 0.6–0.8 *M* concentration levels by procedures mentioned previously.[2,3,5]

Nmr Spectra.—Nmr spectra were obtained on a Varian XL-100-15 spectrometer with accompanying VFT-100-X Fourier transform unit. The line positions for noise-decoupled spectra were read out of the accompanying Varian 620i computer and, after referencing, are accurate to ±0.2 ppm. All halonium ion spectral parameters were measured at -65 to $-70°$ and referenced to carbon disulfide as described in the text. Chemical shifts for the cyclic sulfides and alkanes were measured on 1.0 *M* solutions in carbon tetrachloride at room temperature and were referenced to centered 5-mm tubes of $C_2F_4Br_2$. The $C_2F_4Br_2$ signal was separately shown to be 78.2 ppm upfield from CS_2 in CCl_4 at room temperature. The δ ^{13}C values obtained for the cyclic sulfides and alkanes follow: ethylene sulfide (thiirane), C-2 175.1; trimethylene sulfide (thietane), C-2 166.9, C-3 164.8; tetramethylene sulfide (thiolane), C-2 162.1, C-3 162.9; pentamethylene sulfide (thiane), C-2 163.3, C-3 164.1, C-4 165.7; cyclopropane, 195.4; cyclobutane, 170.0; cyclopentane, 166.9; and cyclohexane, 165.8.[19] Assignments of the various carbon shifts in the sulfur heterocycles was accomplished by heteronuclear hydrogen decoupling while observing the carbon spectrum.

Registry No.—**4**, 22211-89-8; **5**, 22211-90-1; **6**, 22211-91-2; **7**, 33740-96-8; **8**, 33740-97-9; **9**, 33740-98-0; **10**, 33740-99-1; **11**, 22211-92-3; **12**, 23595-67-7; **13**, 22211-93-4.

Acknowledgment.—Support by the National Science Foundation (Grant GP 30683) is gratefully acknowledged.

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

(18) J. W. Larsen and A. V. Metzner, *ibid.*, **94**, 1614 (1972).

(19) We are indebted to Dr. P. M. Henrichs for obtaining some of these values.

Uniparticulate Electrophilic Addition to Alkenylidenecyclopropanes[1]

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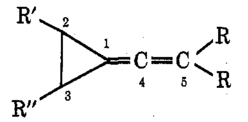
The reaction of a number of substituted isobutenylidenecyclopropanes with chlorosulfonyl isocyanate (CSI) have been investigated for comparison with the reactions of the alkenylidenecyclopropanes with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). In the previous article the cycloaddition reactions of alkenylidenecyclopropanes with PTAD were described, product formation being proposed to occur *via* a concerted process. A new molecular orbital description of the bonding in the alkenylidenecyclopropanes and the transition states for cycloaddition was advanced to account for the mode of reaction and high reactivity. In contrast to the singular mode of reaction of alkenylidenecyclopropanes with PTAD, the reactions with CSI produce both cyclopropane ring-retained (*N*-chlorosulfonyl-β-lactams formed by electrophilic attack at C_5) and ring-opened (five-membered ring *N*-chlorosulfonylimino ethers and *N*-chlorosulfonyl-γ-lactams derived by attack at C_4) products. The ratio of cyclopropane-retained and -opened products is a sensitive function of the number and type of functions attached to the three-membered ring. Product formation is discussed in terms of stabilization of the cationic portion of the dipolar intermediates. It is proposed that the substituent effects on the mode of electrophilic attack arise from stabilization and delocalization of the positive charge developed in the p orbital of C_4 on electrophilic attack at C_5 (which is coplanar with the three-membered ring) with the molecular orbitals of the cyclopropane ring in a manner similar to that described for the ground-state electronic structure of alkenylidenecyclopropanes.



Attack by a nonbridging electrophile on an allene can occur either at the central or the terminal carbon of the cumulene system. Initial bonding at the central carbon produces a nonresonance-stabilized cationic species (path A),[3] the vacant orbital being orthogonal to the proximate π-electron system. Electrophilic attack at a terminal carbon leads to the formation of a vinyl cation (path B).[4] Competition between these two pro-

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(1) (a) Cycloaddition Reactions of Cyclopropane-Containing Systems. IV. For the previous paper in this series see D. J. Pasto, A. F.-T. Chen, and G. Binsch, *J. Amer. Chem. Soc.*, **94**, 1553 (1973). Submitted by A. F.-T. C. in partial fulfillment of the requirements for the Ph.D., University of Notre Dame, 1972. (b) Unsaturated Heterocyclic Systems. LXXXVIII. For the previous paper in this series see L. A. Paquette and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **94**, 632 (1972).

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(3) T. L. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960); K. Griesbaum, W. Naegele, and G. G. Wanless, *ibid.*, **87**, 3151 (1965); W. L. Waters and E. F. Kiefer, *ibid.*, **89**, 6261 (1967).

(4) For a recent review of this subject see M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970). See also S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **93**, 1925 (1971); D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971).