

Table I. Ratio of Longitudinal to Transverse Relaxation Time in Presence of Cu(II)

	T_{1p}/T_{2p}
Acetate	6.9
Chloroacetate	1.1
Bromoacetate	1.9
Glycolate	1.8
Malonate	8.4
Succinate	2.1
Methylamine	350
Dimethylamine	250
Trimethylamine	255
1,2-Diaminoethane	146
Glycinate	108
Sarcosinate CH ₂	49
CH ₃	132
<i>N,N</i> -Dimethylglycinate CH ₂	1.8
CH ₃	2.7
Nitrilotriacetate	0.8
Imidazole H2	21
H(4,5)	48
AMP H8	3.2
H2	5.1

time of the bound paramagnetic ion, τ_s the electron spin relaxation time, A the scalar or hyperfine coupling constant, and r the distance between the paramagnetic ion and the measured nucleus. Since the scalar contribution to T_{1m}^{-1} is negligible compared to the dipolar term it is not included in eq 1.

This communication aims to determine whether the dipolar term of eq 2 dominates the line broadening in the case of rapid chemical exchange. If only the dipolar part contributes to eq 2, both relaxation times depend upon r^6 and the ratio $T_{1p}/T_{2p} = T_{1m}/T_{2m} = \frac{7}{6}$. If either the criterion of rapid exchange or predominant dipolar contribution to eq 2 is not met, the observed ratio will be greater than $\frac{7}{6}$. With fast chemical exchange, 50% scalar and 50% dipolar contributions to eq 2 increase the ratio to $\frac{7}{3} = 2.33$.

We have chosen to determine the ratio T_{1p}/T_{2p} in relatively simple ligands which are not complicated by spin-spin coupling of the measured hydrogens. For each proton only a single resonance corresponding to the weighted average of unbound and bound ligand is observed. Results were obtained in D₂O solutions containing 0.1–0.4 *M* ligand and 10⁻⁵ to 10^{-2.7} *M* Cu(II). The highest concentrations of Cu(II) were employed with the carboxylate ligands, which gave little broadening, and hence the T_{2p} values are less accurate for this ligand class. The pD was chosen such that carboxylic acid ligands were about 75% ionized and amine ligands about half-neutralized. T_{2p}^{-1} and T_{1p}^{-1} values were proportional to Cu(II) concentration. Both T_1 and T_2 relaxation times were determined on a JEOL PFT-100P/EC100 nuclear magnetic resonance spectrometer at 100 MHz and 23°. T_{2p}^{-1} was calculated by multiplying by π the difference of the line width of the free ligand from that found in the presence of added Cu(II). T_{1p}^{-1} values were calculated from the difference of T_1^{-1} values found in the presence and absence of added Cu(II). T_1^{-1} values were accurately ($\pm 10\%$) determined from a 180°– τ –90° pulse sequence. The usual precautions³ were taken and in all cases first-order plots were obtained indicative of exponential decays.

Comparisons of experimentally observed T_{1p}/T_{2p} ratios with the theoretical value of $\frac{7}{6} = 1.17$ tests for dominance of the dipolar term in the fast exchange limit. Perusal of results listed in Table I shows that only in a few cases may the dipolar term of eq 2 be dominant in the fast exchange limit. The dipolar limiting value of 1.17 is obtained only for chloroacetate and nitrilotriacetate. Except for acetate, nonche-

lating carboxylates give values near 2. The higher value for malonate may be ascribed to chelation, which is absent in succinate. Aliphatic amines usually yield high values greater than 40. Carboxylate like values for *N,N*-dimethylglycinate (pD 10.7) and nitrilotriacetate (pD 11.8) suggest that they are bound only as carboxylates at the 200-fold or greater ratio of ligand to Cu(II). The aromatic nitrogens in imidazole and adenosine monophosphate (AMP) also give values of T_{1p}/T_{2p} indicating that line broadening is not determined predominantly by the dipolar mechanism.

The main conclusion of this communication is that the broadening induced by Cu(II) in the proton magnetic resonance spectra of a variety of ligands is generally far from being dipolar determined and thus conclusions concerning the site of Cu(II) attachment based on an assumed r^{-6} dependence require reconsideration. The insignificance of the dipolar mechanism may be due to an important contribution from the scalar term in eq 2 and/or it may occur because the fast exchange limit is not attained. In the latter case an additional term $pq\tau_m\Delta\omega_m^2$ is added to the expression for T_{2p}^{-1} where τ_m is the lifetime of a ligand bound to Cu(II) and $\Delta\omega_m$ is the chemical shift between bound and unbound ligand resonances.¹ Since both the scalar coupling constant A in eq 2 and $\Delta\omega_m$ are in general different for each nucleus on the same ligand, the relative contributions of the two effects require extensive temperature and frequency variation studies for their unraveling. Whatever the outcome to these studies, now underway, predominant contributions to line broadening do not originate in the dipolar mechanism. This conclusion renders suspect arguments of Cu(II) site binding, based on selective broadening, which depend upon assumption of an r^{-6} dependence between Cu(II) and affected nuclei. For ligands undergoing fast or intermediate exchange, the only sure way to invoke the r^{-6} dependence to establish binding sites is to measure T_{1p} and employ eq. 1.

As our most recent experiments suggest that the fast exchange limit is attained for most ligand resonances in Table I, the dominant contributor to line broadening with added Cu(II) is the scalar term of eq 2.

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References and Notes

- (1) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
- (2) I. Solomon, *Phys. Rev.*, **99**, 559 (1955); N. Bloembergen, *J. Chem. Phys.*, **27**, 572 (1957).
- (3) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N.Y., 1971, pp 43–45.

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Onium Ions. XI.¹ The Cyclopentenebromonium Ion, a Bicyclic Three-Membered Ring Halonium Ion

Sir:

Cyclic and acyclic halonium ions have been thoroughly studied in recent years.² Although a series of acyclic, three-membered ring halonium ions have been previously reported,³ related bicyclic halonium ions have not yet been

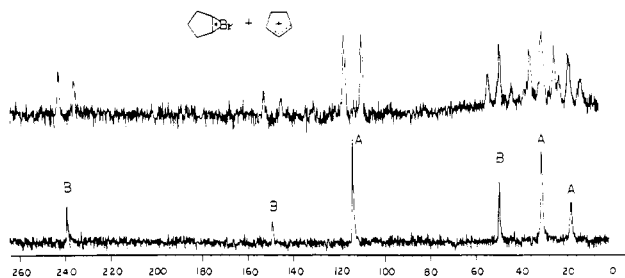
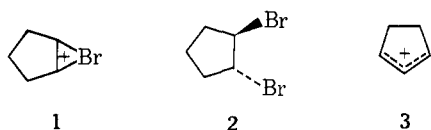


Figure 1. (a) Proton noise-decoupled carbon-13 nmr spectrum of **1** (peaks marked A) and **3** (peaks marked B). (b) Proton coupled carbon-13 nmr spectrum.

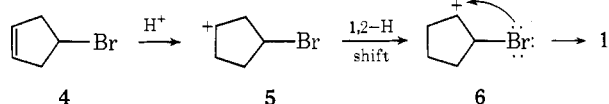
observed. We wish to report now the direct observation of the cyclopentenebromonium ion, the first such bicyclic halonium ions.

The cyclopentenebromonium ion (**1**) was prepared by ionization of *trans*-1,2-dibromocyclopentane in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -120° . The pmr (60 MHz) spectrum of



the ion solution shows a broadened peak at δ 7.32 (two protons) and two broad peaks centered at δ 3.14 (four protons) and 2.50 (two protons). The solution of **1** in $\text{SbF}_5\text{-SO}_2\text{ClF}$ also shows the presence of the related cyclopentenyl cation **3**.⁴ When the solution was slowly warmed to -80° , **1** gradually and cleanly transformed into the allylic ion **3**.⁴ Ion **3** present initially in solution of **1** might be formed due to local overheating during preparation. This reaction sequence is in accordance with our previously reported ionization of **2** in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -78° where only the allylic ion **3** was observed.⁴ Apparently the bromonium ion **1** is not stable at this higher temperature and was completely converted into allylic ion **3**.

The bromonium ion **1** was also obtained *via* protonation of 4-bromocyclopentene (**4**) in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ solution at -120° .

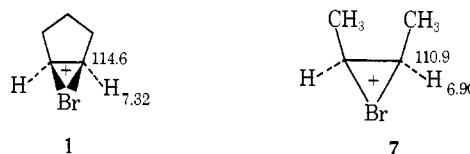


4 underwent protonation in $\text{FSO}_3\text{H-SbF}_5$ to first give 3-bromocyclopentyl cation **5**, which then underwent a 1,2-hydride shift to give 2-bromocyclopentyl cation **6**. Subsequently, **6** gave **1** *via* neighboring bromine participation as in the case of direct ionization of 1,2-dibromocyclopentane (**2**).

In order to further ascertain the structure of cyclopentenebromonium ion (**1**), we also have obtained its carbon-13 nmr spectrum.⁵ The proton noise-decoupled ^{13}C spectrum (Figure 1a) shows three carbon resonances at $\delta(^{13}\text{C})$ 114.6 (doublet, $J_{\text{C-H}} = 190.6$ Hz), 31.8 (triplet, $J_{\text{C-H}} = 137.6$ Hz), and 18.7 (triplet, $J_{\text{C-H}} = 134.0$ Hz). In addition the cmr spectrum of **1** shows three additional minor peaks which exactly correspond to those reported for the cyclopentenyl cation **3**.⁶ The cmr assignments for ion **1** were made with the aid of the proton coupled cmr spectrum (Figure 1b). The bicyclic structure of the bromonium ion **1** is, therefore, firmly established.

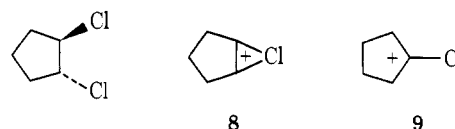
It is instructive to compare both proton and carbon shifts of **1** with those of suitable model ions. The most closely related known acyclic bromonium ion containing a three-

membered ring is the *cis*-1,2-dimethylethylenebromonium ion (**7**).³ The chemical shift for the two carbon atoms where bridging takes place in **7**^{2a} is found at $\delta(^{13}\text{C})$ 110.9 which is



in good accordance with that in **1** (114.6). The proton shifts for the two equivalent olefinic-type protons in both ions **1** and **7** are also similar.³

Acyclic three-membered ring chloronium ions are known.^{2,3} Consequently, we have attempted to prepare the cyclopentenechloronium ion *via* ionization of *trans*-1,2-dichlorocyclopentane in $\text{SbF}_5\text{-SO}_2\text{ClF}$ at -120° . We have obtained, however, instead of the chloronium ion **8**, only the 1-chloro-1-cyclopentyl cation (**9**).⁷ Apparently, the partici-



ipation of the smaller chlorine atom could not effectively compete with the fast 1,2-hydride shift forming the tertiary ion, **9**. The larger bromine atom, however, preferentially participates with the neighboring electron-deficient center forming the bicyclic bridged ion **1**.

The rearrangement of cyclopentenebromonium ion (**1**) to allylic cyclopentenyl cation **3** can take place *via* thermal ring-opening to give 2-bromocyclopentyl cation (**6**), which can deprotonate to give 3-bromocyclopentene. Subsequent ionization of the latter would give the allylic ion **3**.^{4,7}

A comprehensive report on our continued study concerning bicyclic halonium ions and their significance to addition and rearrangement reactions will be published.

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References and Notes

- (1) Part X. G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *J. Amer. Chem. Soc.*, **96**, 3565 (1974).
- (2) For a review, see G. A. Olah, "Halonium Ions in Organic Chemistry," Wiley-Interscience, New York, N.Y., in press.
- (3) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).
- (4) G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3544 (1972).
- (5) Carbon-13 nmr spectra were obtained by Fourier-transform method using a Varian XL-100 nmr spectrometer equipped with a variable temperature probe. External tetramethylsilane (TMS, capillary) was used as reference for carbon shifts.
- (6) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **94**, 6434 (1972).
- (7) G. A. Olah, G. Liang, and Y. K. Mo, *J. Org. Chem.*, **39**, 2394 (1974).

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Graphite Electrolytic Lamellar Reagents in Organic Chemistry. Esterifications in the Presence of Graphite Bisulfate

Sir:

The chemical behavior of molecules intercalated in graphite^{1,2} may differ in various ways from that of the free or bulk reagents, as was observed in the case of bromine³