

alyst (20 mg) the corresponding yields were 32.7 and 30.5%, respectively.

When experiments with α -diazacetophenone, diazomethane, and diazofluorene were repeated without the presence of tetraphenylethylene, *no* cyclopropanation products were detected.

In the tetraphenylethylene-catalyzed cyclopropanations with diazoacetophenone, diazomethane, and diazofluorene, no paramagnetic species were detected by esr spectroscopy during the reaction or after decomposition of the diazo compound was complete. Thus the relationship between these reactions and the tetraphenylethylene-catalyzed decomposition of diphenyldiazomethane remains to be established by detailed kinetic studies and trapping experiments.

The catalyst employed in our experiments is commercial tetraphenylethylene (Aldrich) purified by recrystallization followed by column chromatography. Since the synthesis of tetraphenylethylene normally employs copper metal,¹⁷ we explored the possibility that a copper impurity was responsible for the observed decomposition of diazo compounds. Decomposition of diazo compounds by copper complexes present in only 10^{-2} *M* ratio has been reported.¹⁸ Analysis of our purified tetraphenylethylene by atomic absorption spectroscopy indicated a copper content of 0.01 weight %. When a quantity of cupric chloride (the most likely form for a copper impurity in tetraphenylethylene) equivalent to ten times the impurity found in tetraphenylethylene was employed as a catalyst for diphenyldiazomethane decomposition, the first half-life of the reaction is greater than four times that observed with tetraphenylethylene. Also the rate of the copper-catalyzed reaction was the same in the presence and absence of air. Copper was definitely precluded as the active catalyst when a sample of tetraphenylethylene prepared by Meyers *via* a copper-free synthesis¹⁹ showed catalytic properties identical with those of commercial material.

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- The reaction described occurs in all solvents thus far employed: tetrahydrofuran, benzene, methylene chloride, and dimethoxyethane.
- Electrolytic oxidation of an acetonitrile solution 0.002 *M* in benzophenone azine with 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte was carried out at 2.0 V in a vacuum electrolysis cell designed by S. I. Weissman and C. Cheng employing a platinum anode and mercury cathode.
- At room temperature the first half-life for decomposition of Ph_2CN_2 in a tetrahydrofuran solution *under air* 0.015 *M* in both Ph_2CN_2 and $\text{Ph}_2\text{C}=\text{CPh}_2$ is 23 hr. In a refrigerator, decomposition was not complete after 2 weeks, compared to the 2 hr required for a similar degassed solution.
- These experiments were carried out by adding the metal salt to degassed solutions of diphenyldiazomethane in tetrahydrofuran. The resulting green solutions were immediately decanted directly into esr sample tubes without exposure to air and the spectra recorded. In the metal-containing systems the esr signal of the azine radical cation persists only briefly, disappearing within minutes (Zn) to hours (Cu^{II}).
- No charge-transfer complex between diphenyldiazomethane and tetraphenylethylene has been detected by optical absorption spectroscopy, the experiments having been carried out without degassing on solutions 10^{-3} *M* in both compounds. Direct electron transfer from Ph_2CN_2 to $\text{Ph}_2\text{C}=\text{CPh}_2$ is too endothermic (ca. 3 eV) to be considered likely. The esr spectrum of the radical anion of tetraphenylethylene has not been observed in our experiments. The predominant counterion is probably the dianion of tetraphenylethylene, formed by disproportionation of the radical anion.
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- Cuprous chloride catalyzed decomposition of diphenyldiazomethane in the presence of cyclohexene, morpholinocyclohexene, 1-octene and *trans*-4-methyl-2-pentene at room temperature produced in all cases high yields of benzophenone azine but *no* detectable cyclopropanes. H. Nozaki, S. Morituti, M. Yamabe and R. Noyori, *Tetrahedron Lett.*, 59 (1966), have reported the copper acetate catalyzed decomposition of diphenyldiazomethane in the presence of the enamine morpholinocyclohexene at the temperature of refluxing benzene to give a 62% yield of the cyclopropanation product. We repeated this experiment at room temperature and obtained no cyclopropane but did isolate $\text{Ph}_2\text{C}=\text{CPh}_2$ in 17.4% yield and azine in 58.7% yield. Copper catalyzed decomposition of diphenyldiazomethane in refluxing cyclohexane leads to the formation of azine but no carbon-hydrogen insertion (private communication from L. T. Scott; *cf. ref 4*).
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Cautions Concerning Uses of Copper(II) Selective Broadening in Nuclear Magnetic Resonance Spectroscopy for Determination of Ligand Binding Sites

Sir:

Sites of Cu(II) binding to molecules such as nucleic acid bases, histidine and derivatives, and peptides have often been characterized by selective broadening in proton magnetic resonance spectra of ligand hydrogens located nearest to Cu(II). Typically the ligand is present in a 100-fold or greater excess over Cu(II). To apply the method successfully to small molecules, two criteria must be met: there must be rapid chemical exchange of Cu(II) among all sites and there must be no scalar coupling to contribute to line broadening so that only the dipolar contribution with its inverse sixth power dependence of distance between paramagnetic ion and affected nuclei prevails.

In the case of rapid chemical exchange and in the absence of significant outer sphere effects, the inverse spin-lattice and transverse relaxation times due to the presence of paramagnetic ion become¹

$$T_{1p}^{-1} = pqT_{1m}^{-1}$$

and

$$T_{2p}^{-1} = pqT_{2m}^{-1}$$

where *p* is the ratio of molar concentrations of metal ion to ligand and *q* is the average number of ligands bound in an identical way. Thus $T_{1p}/T_{2p} = T_{1m}/T_{2m}$. The relaxation times of nuclei bound to paramagnetic ions may be described by the Solomon-Bloembergen equations² which for Cu(II) and protons on small ligands at 100 MHz become

$$T_{1m}^{-1} = 6a\tau_r r^{-6} \quad (1)$$

$$T_{2m}^{-1} = 7a\tau_r r^{-6} + bA^2\tau_s \quad (2)$$

where *a* and *b* are a collection of constants for the dipolar and scalar parts, respectively, τ_r is the rotational correlation

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 D_2O 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 $180^\circ\text{-}\tau\text{-}90^\circ$ 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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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