

Organic and Biological Chemistry

Nuclear Magnetic Resonance Investigation of Secondary Valence Forces. I. Intramolecular π Coordination in Aralkylmercury Compounds

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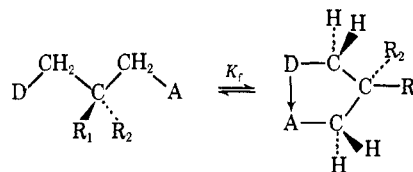
Abstract: A general approach to the study of weak donor-acceptor interactions is described, based on conformational analysis of a flexible intramolecular model by nuclear magnetic resonance spectroscopy. The major feature of this model is a centrally located asymmetric center, which allows strong magnetic nonequivalence in flanking methylene groups to develop when intramolecular coordination is present. Applications of this approach to a series of γ -arylpropylmercury compounds reveals that π electrons of a benzene ring are involved in coordinate bonding with the mercury atom.

We wish to discuss a general approach to the investigation of relatively weak ground-state electronic interactions in solution, and to report on the application of this method to a study of mercury-arene coordination in a series of organomercury compounds. The theoretical background and many of the experimental considerations which relate to the general problem have been lucidly reviewed by Leffler and Grunwald² and by Arnett,³ among others; the specific disadvantages of standard spectroscopic methods which make such an alternative approach desirable have been discussed by several authors.⁴

Our approach is based on the "chelate effect"—the greatly enhanced stability of intramolecular relative to intermolecular coordinate bonds in metal complexes. It is well known that the chelate effect, except in certain cases where ring strain can lead to ligand rehybridization, is due almost entirely to a favorable entropy change. Expression of the formation constant K_f for a complex as $R \ln K_f = -\Delta H_f/T + \Delta S_f$ emphasizes the leveling effect of a large negative entropy term on weak coordinate bonds at ordinary temperatures. The dominant contributions to this entropy decrease in intermolecular equilibria are losses of translational and external-rotational modes of freedom, which lead to the conclusion that weak coordination effects could best be studied by considering a strain-free intramolecular model in which these entropy contributions are absent.

The choice of an experimental method for the determination of K_f becomes much more limited in a unimolecular equilibrium, however, since donor and acceptor cannot be physically separated and classical distribution methods of analysis are inapplicable. Observable properties of the donor-acceptor bond itself, such as charge transfer or vibrational absorption bands,

can of course still be used, and a study of the ultraviolet and far-infrared spectra of some of the compounds reported herein is indeed planned. However, these techniques suffer the major disadvantage that each new type of interaction to be studied must be approached as a brand new experiment, and we feel that they are best suited to examination of the electronic details of already-established interactions. In any case, we have chosen in this investigation to avoid direct confrontation with specific donor-acceptor pair properties, particularly those involving excited electronic or vibrational states, and adopt a method based on conformational analysis of a standard three-carbon chain to which a large variety of donor-acceptor pairs can be attached. Since steric factors in the standard chain can be kept nearly constant (and, if small enough to be considered roughly additive, can be estimated from excellent recent data⁵), changes in the resulting conformational equilibrium between five- or pseudo-five-membered ring and open-chain forms will be to a rather good approximation a sensitive function of the donor-acceptor bond strength alone.



Analysis by nmr is facilitated by making the central carbon atom of the chain asymmetric (when $D \neq A$), so that both of the remaining methylene groups can display magnetic nonequivalence. In general, the appearance of temperature-dependent magnetic nonequivalence in proton spectra can be taken as an indication of unequal conformer populations,⁶ and very pro-

(1) National Defense Education Act Predoctoral Fellow, 1965-1966.

(2) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapters 2 and 3.

(3) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 203 (1963).

(4) T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967); S. W. Ross, *ibid.*, **87**, 3032 (1965), and references cited by these authors.

(5) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *ibid.*, **89**, 1135 (1967).

(6) (a) G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964), and references cited therein. See, however, (b) E. I. Snyder, *ibid.*, **85**, 2624 (1963). We believe that in the light of more recent research, Snyder's data show much evidence of conformational effects.

nounced nonequivalence (*i.e.*, of a similar order of magnitude to that encountered in cyclic compounds with the same functional groups) normally suggests a unique conformational energy minimum. It is not immediately evident, of course, which conformation is preferred; however, if it can be shown that an observed conformational preference arises from intramolecular coordination rather than from steric or dipolar repulsions, the gross conformation is incidentally established and need only be verified if desired by examination of appropriate spin-spin coupling data.⁵ In the present work, we have made use of strongly angular-dependent long-range heteronuclear coupling⁷ and of the well-established anisotropic shielding effect of an aryl group⁸ for conformational verification.

Demonstration that intramolecular coordination is responsible for restricted rotation in a particular model can be achieved by applying a combination of simple experimental criteria. Since much remains to be understood about the factors which contribute to the chemical shift, we have been hesitant to label any single test unequivocal,^{6b} but taken in concert the following considerations do seem to preclude any other reasonable interpretation. (a) Residual steric effects: substitution of an inert substituent of similar size⁵ for donor and acceptor in turn should result in a dramatic attenuation, if not total disappearance, of spectral evidence for strong conformational preference. (b) Substituent effects: electron-donating and -attracting substituents or ligands bonded (in sterically inconsequential positions) to the donor and/or acceptor should cause the expected enhancement or diminution of K_f . (c) Solvent effects: solvents of higher basicity should compete with the donor substituent for coordination at the acceptor site, leading to a decrease in K_f . Care must be exercised in the choice of solvents, however, since it has been shown that a correlation between magnetic nonequivalence and solvent dielectric constant exists in certain compounds which appears to be, at least in part, independent of conformational considerations.^{6b,9} (d) Concentration dependence: decreasing concentration of an inert solvent should result in a nonlinear increase in K_f as competition from intermolecular interactions diminishes.¹⁰ This highly revealing experiment is of course a classic test for intramolecular hydrogen bonding in infrared spectra, and can in principle be used to obtain a quantitative assessment of relative donor-acceptor bond strengths. (e) Temperature dependence: A demonstration of the temperature dependence of spectral criteria should be made in order to verify the existence of a preferred conformation, though it indicates nothing in itself about the nature of the conformational energy difference. In the absence of spectral data for either of the limiting conformations of a particular model, the determination of ΔH_f for a given

The apparent similarity of some of the spectral behavior of our compounds and his, however, makes it clear that geminal chemical shift data must be interpreted with considerable caution.

(7) (a) A. F. Kiefer and W. L. Waters, *J. Amer. Chem. Soc.*, **87**, 4401 (1965); (b) M. M. Kreevoy and J. F. Schaefer, *J. Organometal. Chem.*, **6**, 589 (1966); (c) F. A. L. Anet, *Tetrahedron Lett.*, 3399 (1964).

(8) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958). This criterion has recently been applied to a study of intramolecular coordination in 2-arylethyl *p*-toluenesulfonates: M. D. Bentley and M. J. S. Dewar, *Tetrahedron Lett.*, 5043 (1967).

(9) G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1058 (1965).

(10) E. D. Baker, U. Liddel, and J. N. Shooley, *J. Mol. Spectrosc.*, **2**, 1 (1958); M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958).

donor-acceptor bond (rather than the simple conformational free energy difference ΔG_f) from variable-temperature measurements is not a trivial problem, since the equal-entropy approximation applicable to simpler conformational equilibria^{5,11} cannot be assumed to be valid. It is often possible, however, to deduce quite reasonable nmr values for one of the limiting conformations (generally the open-chain "steric" conformer), after which determination of the donor-acceptor bond strength is relatively straightforward; this quantitative treatment will be the subject of a later publication.

As a general approach to the study of weak secondary valence forces, this intramolecular model has two obvious limitations: both donor and acceptor must be strongly bonded to the chain (though not necessarily to a carbon atom), and coordinate bond angles and distances are somewhat restricted by the steric constraints of the model. These considerations prohibit the study of many chemical species in their "natural" unbonded states and also make the scheme inappropriate for, *e.g.*, linear donors such as the cyano group. Nonetheless, since the approach is fundamentally independent of the nature of the interaction being studied, it appears to hold considerable promise in exploring relatively weak potential effects, such as that described below, which have escaped detection in intermolecular systems because of the unfavorable entropy loss, or whose presence in complex molecules is obscured by more readily detectable phenomena.

Results

The nmr spectra of 3-phenyl-2-methyl-2-methoxypropylmercuric chloride (**1**) and 3-phenyl-2-methyl-2-methoxypropyl bromide (**2**) in carbon tetrachloride are shown in Figure 1. Assignment of the quartet at higher field in **1** to the CH_2Hg protons is verified by the large (188, 207 Hz) mercury-proton coupling constants associated with $^{199}\text{Hg-C-H}$ splitting.¹² The greatly diminished methylene group nonequivalence in the bromo compound **2** suggests that there is no clear-cut conformational energy minimum for this molecule, an observation which is consistent with the expected similar steric requirements of methyl, benzyl, and bromomethylene groups in acyclic compounds.⁵ Other evident features of the spectrum of **1** which point to a *gauche, gauche* Hg-C-C-C-Ar conformation include the large $^{199}\text{Hg-C-C-CH}_3$ coupling (39 Hz, *trans*, compared to ≤ 5 Hz for the *gauche* $^{199}\text{Hg-C-C-CH}_2$ coupling)⁷ and the perturbation of the aromatic proton resonance. Since Whitesides and coworkers' careful study of conformational energies in substituted ethanes⁵ have shown that HgCl and Br substituents are very nearly the same effective size in acyclic systems (if anything, Br appears to be slightly larger), it is clear that something other than a simple steric effect must be responsible for these dissimilar spectra.

Tables I-V summarize the results of experiments designed to rule out other possible alternatives by providing positive evidence for the existence of an intramolecular coordinate bond between the aromatic ring and the mercury atom in **1**. These tables correspond to the application of criteria a-e above, respectively.

(11) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965, Chapter 1.

(12) P. R. Wells and W. Kitching, *Tetrahedron Lett.*, 1531 (1963).

Table I. Donor–Acceptor Effects on Magnetic Nonequivalence and ^{199}Hg –C–C–CH₃ coupling in $\text{RCH}_2\text{C}(\text{CH}_3)(\text{OCH}_3)\text{CH}_2\text{X}$

R	X	$\Delta\nu_{\text{CH}_2\text{R}^a}$	$\Delta\nu_{\text{CH}_2\text{X}}$	J_{HgCCCH_3} , Hz
C ₆ H ₅	HgCl	29	14	39
C ₆ H ₅	Br	4.2	<3	...
CH ₃	HgCl	<3	<3	20
CMe ₃	HgCl	5.4	7.3	16
NMe ₂	HgCl	39	42	46

^a Chemical shift between methylene protons in hertz at 60 MHz.

The data of Table I show that replacement of either donor (phenyl) or acceptor (chloromercuri) substituent by an inert group results in a marked attenuation of spectral evidence for conformational preference, even in the case of the *t*-butyl group. A strongly preferred conformation is particularly evident from the spectrum of the dimethylamino derivative, as would be expected from the basicity of this substituent. The same effect has been noted for the chloropalladium adduct of methallyldimethylamine, and has been ascribed to intramolecular coordination.¹³

It is clear from the data of Table II that an electron-donating *para* substituent (e.g., CH₃O) on the benzene ring increases conformational preference, while an electron-attracting substituent (e.g., CF₃) has the opposite effect. Likewise, the effect of varying the mer-

Table II. Substituent Effects on Arene–Mercury Coordination in $\text{ArCH}_2\text{C}(\text{CH}_3)(\text{OCH}_3)\text{CH}_2\text{HgX}$

Ar	X	$\Delta\nu_{\text{CH}_2\text{Ar}}$, Hz	$\Delta\nu_{\text{CH}_2\text{Hg}}$, Hz	J_{HgCCCH_3} , Hz
<i>p</i> -CH ₃ OC ₆ H ₄	Cl	38	20	44
Mesityl	Cl	26	20	48
C ₆ H ₅	Cl	29	14	39
<i>p</i> -ClC ₆ H ₄	Cl	26	14	37.5
<i>p</i> -CF ₃ C ₆ H ₄	Cl	23	12.5	35
C ₆ H ₅	OAc	19.5	7.8	34
C ₆ H ₅	Br	30.5	16.5	40
C ₆ H ₅	I	32.5	18	<i>a</i>
C ₆ H ₅	CN	39	23	48

^a Mercury satellites too broad to measure.

cury ligand parallels the association constants of these ligands with methylmercury,¹⁴ indicating that strongly bound ligands apparently increase the electron-accepting capacity of a mercury atom.

It can be seen from the data of Table III, in which solvents are listed in order of increasing basicity, that a direct correlation of spectral criteria with this property is observed, but no corresponding relationship to solvent dielectric constant^{6b,9} or any other obvious molecular property. The effect of oxygenated solvents is not large, which may reflect the fact that mercury has little affinity for oxygen bases.¹⁴ In fact, since dioxane showed somewhat anomalous behavior in an earlier study of magnetic nonequivalence,⁹ the chemical shift trend for the first five solvents of Table III might be considered to fall within the “normal” range;^{6b} however, pyridine clearly does not.

A small, linear increase in geminal chemical shifts upon dilution (Table IV) might be ascribed to a bulk

(13) A. C. Cope, J. M. Kliegman, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **89**, 287 (1967).

(14) R. B. Simpson, *ibid.*, **83**, 4711 (1961).

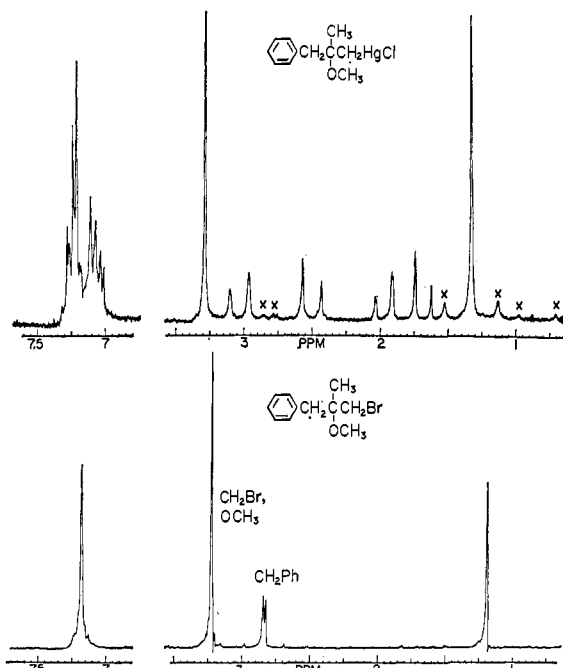


Figure 1. Proton nmr spectra of **1** and **2** (100 MHz). In the upper spectrum, observable ^{199}Hg satellites are marked “X,” and the aromatic multiplet is recorded at increased gain.

solvent effect,^{6b} but the observed increase is clearly non-linear, and is characteristic of the presence of competing second- or higher order solute–solute interactions.¹⁰

Table III. Solvent Effects on Intramolecular Coordination in $\text{p-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)(\text{OCH}_3)\text{CH}_2\text{HgCl}$ (**3**)

Solvent	$\Delta\nu_{\text{CH}_2\text{Ar}}$, Hz	$\Delta\nu_{\text{CH}_2\text{Hg}}$, Hz	J_{HgCCCH_3} , Hz	ϵ^{25° solvent ^a
CCl ₄	39	22	44	2.24
C ₆ H ₆	38	17	42	2.28
C ₆ H ₅ NO ₂	32	13	42	36.1
CH ₃ OH	28	12	40	32.7
Dioxane	25	10	36	2.21
Pyridine	15	4	32	12.5

^a Reference 9.

Table IV. Concentration Dependence of Spectral Criteria for Compound **1**

Concn, %	$\Delta\nu_{\text{CH}_2\text{Ar}}$, Hz	$\Delta\nu_{\text{CH}_2\text{Hg}}$, Hz	J_{HgCCCH_3} , Hz
25.0	28.0	13.5	38.0
10.0	29.0	14.0	39.0
5.0	30.5	15.2	39.5
2.5	32.7	16.7	40.3

The strong temperature dependence of both chemical shifts and coupling constants shown in Table V establishes that a conformational energy difference is present. Though no attempt was made to determine the donor–acceptor bond strength from these data, the free energy difference can be estimated⁵ as about 1.5 kcal/mol by using the magnetic nonequivalence values of compound **2** and J_{HgCCCH_3} from analogous aliphatic mercury compounds as rough models for a noninteracting system.

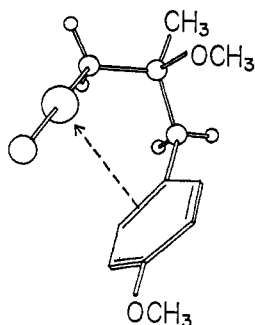


Figure 2. The preferred conformation of 3-(*p*-methoxyphenyl)-2-methyl-2-methoxypropylmercuric chloride (**3**) resulting from intramolecular mercury–arene coordination.

In addition to the methylene group nonequivalence and long-range mercury–proton coupling data given in Tables I–V, other spectral properties show evidence for the proposed chelate effect. Perturbation of the aromatic proton pattern, already noted in Figure 1, is

Table V. Temperature Dependence of Spectral Criteria for Compound **3**^a

Temp, °C	$\Delta\nu_{\text{CH}_2\text{Ar}}$, Hz	$\Delta\nu_{\text{CH}_2\text{Hg}}$, Hz	J_{HgCCCH_3} , Hz
40	37.9	19.6	44.0
15	39.6	20.5	45.5
–10	41.6	21.6	46.6
–40	44.7	22.9	48.0

^a In CDCl₃.

a general phenomenon; for example, $\Delta\nu_{ortho}$ for compound **3** is decreased to 0.14 ppm from 0.27 ppm in the parent *p*-methallylanisole. It is the protons *ortho* to the alkyl side chain which undergo the largest shift. Long-range proton–proton coupling between the low-field half of each methylene quartet, which is a striking spectral feature of 3-dimethylamino-2-methoxy-2-methylpropylmercuric chloride (see Table I), is also present in several of the aralkylmercury compounds, and can be observed in the high-field quartet of compound **1**. (It is obscured by benzylic coupling in the low-field quartet.) Resolvable proton–proton coupling through four σ bonds generally occurs only in cyclic or other conformationally rigid structures.

The chemical shifts of C-methyl and CH₂Hg protons in the aromatic series also support the proposed conformation, based on the calculated benzene anisotropic shielding values of Johnson and Bovey:⁸ the former resonances are shifted 0.07–0.22 ppm to *lower* field, and the latter 0.25–0.58 ppm to *higher* field, relative to analogous aliphatic oxymercurials. Finally, a recently completed X-ray crystallographic study of compound **3** by Stout and Singh¹⁵ shows the structure in the crystalline state to be precisely that shown in Figure 2, with the mercury atom located 3.05 Å above one of the benzene π bonds. The C–Hg–Cl bond angle is apparently bent slightly from the normal 180°, a possible consequence of secondary coordination. Though this result does not in itself constitute proof that the same conformation is favored in solution, it is certainly reassuring.

(15) G. H. Stout and I. Singh, results to be published.

Discussion

We believe there can be little doubt that 3-arylpropylmercury compounds exist in solution largely as intramolecular π complexes. In view of the high reactivity of mercuric salts toward olefins, and of the analogous structures of benzene complexes with salts of group IB metals,¹⁶ it is reasonable to expect that the mercury atom should be situated above the edge of the ring, rather than over the center as in bisbenzenechromium and its relatives. The retained AA'BB' symmetry of the aromatic multiplet in **3** requires that rotation of the aryl group in solution be rapid on the nmr time scale, which is consistent with an estimated conformational energy difference of 1–2 kcal/mol. The somewhat irregular spectral values observed for the mesityl derivative (Table II) are also best explained by such a "localized" π complex; the *o*-methyl groups interfere with free rotation of the aliphatic methoxyl group in the conformation of Figure 2, forcing the molecule to adopt a slightly more symmetrical conformation in which the benzylic protons become more nearly equivalent with respect to the arene ring, and the C-methyl group more precisely *trans* to mercury.

Although mercury π complexes with olefins and acetylenes were first proposed many years ago and a large body of evidence supporting their existence as reaction intermediates has accumulated, no authentic example of a stable π complex has been reported, probably because of the strong tendency of mercury to form stable σ bonds to carbon. We have recently described evidence that the intermediate in oxymercuration of allenes has a bridged, σ -bonded structure.¹⁷ Bis(cyclopentadienyl)mercury was originally proposed to have conventional (though labile) carbon–metal σ bonds,¹⁸ though it has more recently been suggested that bis(π -allyl) bonding may be involved;¹⁹ in any case, it is clear that the compound is not a metallocene. In the crystalline complex of benzene with hexathiocyanatocobaltdimercury, C₆H₆CoHg₂(SCN)₆, there appear to be two mercury atoms associated with each benzene molecule,²⁰ but the mercury–carbon distances (>3.5 Å) are in the ordinary van der Waals range, and it has not been established that π bonding is responsible for the stability of this adduct.

It is not immediately obvious what the chemical consequences of mercury–arene coordination in organomercurials should be. *A priori*, one might expect that π -electron donation to mercury would tend to labilize the carbon–mercury σ bond toward electrophilic substitution and deoxymercuration, but brief exploratory experiments provide no support for this idea; if anything, the opposite seems to be true. The corollary, that π coordination should strengthen the σ bond toward nucleophilic attack has not been investigated. There is considerable evidence, however, indicating that coordinate π bonding has a marked stabilizing effect on carbon–metal σ bonds in general, and indeed

(16) H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, "Benzenoid-Metal Complexes," The Ronald Press Co., New York, N. Y., 1966, Chapter 1.

(17) W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967).

(18) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(19) F. A. Cotton, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **9th**, Houston, 213 (1966).

(20) R. Grønbaek and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 1889 (1964).

is in many cases essential for the existence of σ organometallics as discrete molecular species.²¹ Since mercury is uniquely capable of facile displacement by either electrophilic or nucleophilic reagents, a comparative kinetic study of these two types of reaction might yield valuable clues to the nature of mercury-arene bonding in these and related compounds. The solvolysis rates of γ -arylpropylmercuric perchlorates would be of particular interest in view of the exceptional sensitivity of this reaction to electronic effects.²²

Subsequent work in this laboratory has revealed that intramolecular coordination in organomercury compounds is remarkably general. Olefinic π bonds, as might be expected, complex strongly with mercury, as do a large number of n -electron donors. The following paper reports an investigation of intramolecular mercury-halogen interaction. These studies are currently being extended to other metals.

Experimental Section

Materials. All compounds used in this work were prepared by standard procedures, or purchased. Mercury compounds were

(21) G. E. Coates and F. Glockling in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 426 ff.

(22) F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **85**, 367 (1963), and preceding papers in this series. It has recently been reported that the solvolysis of 3-phenylpropylmercuric perchlorate in acetic acid is slower than that of n -butylmercuric perchlorate by a factor of 2.0 at 100°: R. J. Ouellette and R. D. Robins, *Tetrahedron Lett.*, 397 (1968). The rate ratio for the corresponding p -bromobenzenesulfonate esters under the same conditions is 1.24: R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957).

prepared by oxymercuration of the corresponding alkene with reagent grade mercuric acetate in anhydrous methanol followed by anion exchange and recrystallization as described previously.¹⁷ The arylalkenes were prepared by addition of 3-chloro-2-methylpropene (methallyl chloride) to the appropriate aryl Grignard reagent in ether. Methallyldimethylamine was prepared by the procedure of Cope, *et al.*²³ Compound **2** was obtained by reaction of an equimolar quantity of bromine with compound **1** in carbon tetrachloride, and independently by addition of bromine to methallylbenzene in methanol followed by treatment with methanolic silver nitrate. Polar solvents used for nmr spectra (Table III) contained less than 0.2% water or other impurities.

Spectra. Nuclear magnetic resonance spectra were measured using Varian A-60 or HA-100 nmr spectrometer systems. The data of Tables I-V were obtained originally at 60 MHz; those for which any uncertainty existed due to peak overlap, etc., were subsequently redetermined at 100 MHz and the chemical shifts multiplied by 0.60. Since the values determined at 60 MHz were read directly from the recorded spectra, they have in most cases been rounded off to the nearest 1.0 Hz. All spectra were determined on approximately 10% solutions of sample in carbon tetrachloride at an ambient probe temperature of 42°, unless otherwise noted. Subambient temperatures were measured by the standard ethylene glycol-methanol calibration.

Acknowledgments. We wish to thank Miss Paula Yano and Mr. Jeffrey Carter, participants in a National Science Foundation High School Science Apprenticeship program during summer 1965, for experimental assistance in the preparative work, and Dr. Wolfgang Gericke for recording some of the 100-MHz spectra. We are grateful to the National Institutes of Health for partial support of this research, including funds for purchase of the A-60 and HA-100 spectrometers under Grants GM 10413 and GM 14533-01, respectively.

(23) A. G. Cope, T. T. Foster, and P. H. Towle, *ibid.*, **71**, 3932 (1949).

Nuclear Magnetic Resonance Investigation of Secondary Valence Forces. II. Intramolecular Mercury-Halogen Coordination in 3-Halopropylmercury Compounds

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Abstract: Analysis of the nmr spectra of several compounds with the general structure $XCH_2C(CH_3)(OCH_3)-CH_2HgY$ is carried out with variation of X, Y, solvent, concentration, and temperature. Chemical shift and spin-coupling data are interpreted in terms of an intramolecular donor-acceptor interaction between the electron-pair donor atom X and the mercury atom. Both chloro and bromo substituents are found to form weak coordinate bonds with mercury; $\Delta H_{Hg \cdots Br}$ is estimated to be of the order of 1 kcal/mol. A "conformational titration" is described, in which methylene group magnetic nonequivalence is monitored as a function of concentration of an added base which can displace the intramolecular donor. The dependence of J_{HgCCCH_3} on dihedral angle and the strengths and weaknesses of the general experimental model are discussed briefly. An example of stereospecific HOCH spin coupling in a CH_2OH group is reported.

Although alkyl halides—particularly chlorides and bromides—are typically described as neutral compounds with negligible specific valence interactions in solution, a variety of studies have shown that this class of compounds can exhibit weak to moderate basicity, depending on the type of Lewis acid involved. Most of these investigations have been concerned with

possible intermediates in reactions in which the carbon-halogen bond is ultimately broken, particularly Friedel-Crafts and similar Lewis acid catalyzed alkylations.¹ In general, a distinction must be made between thermo-

(1) For discussion and leading references, see G. A. Olah, "Friedel-Crafts and Related Reactions," Interscience Division of John Wiley and Sons, Inc., New York, N. Y., Vol. I, 1963, and Vol. IV, 1965.