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 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.

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[21] G. E. Coates and F. Glocking 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).

[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-

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[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.

dynamic acidity or basicity in a metathetic equilibrium $X\text{–}A + :B\text{–}Y \rightleftharpoons A{:}B + X\text{–}Y$ and that involved in ground-state coordination, $X\text{–}A + :B\text{–}Y \rightleftharpoons X\text{–}A{:}B\text{–}Y$; these two types of reaction may or may not possess a common energy surface. The continuing work of Olah and his coworkers has, in addition to its impact on carbonium ion theory, substantially clarified the relationship of Lewis acidity and molecular composition in displacement equilibria and provided reliable criteria for distinguishing the above two reaction types in strongly interacting systems.[2] We have fixed our attention on interactions of the second type, which do not ordinarily result in bond fission but which may serve as transient binding mechanisms for enzyme–substrate complexes and have other important chemical and physical consequences.

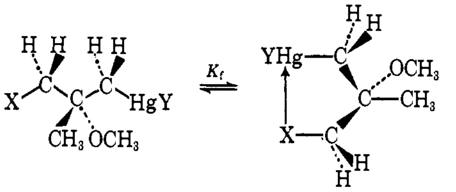
Ground-state coordination between alkyl halides and Lewis acids which does not lead to metathesis has received relatively little attention. The results which have been reported[1] depend strongly on the nature of the experimental methods used to obtain them, and the significance of much of the older data seems questionable. Even hydrogen-bonding interactions, which lend themselves to relatively facile investigation by infrared spectroscopy, are currently a source of controversy: the enthalpy values originally assigned[3] by application of the linear ΔH *vs.* $\Delta\nu_{\mathrm{OH}}$ correlation (Badger's rule)[4] were subsequently revised after more careful thermodynamic analysis[5] and these in turn have recently been reported to be in serious disagreement with calorimetric values (*e.g.*, by a factor of 4 for the phenol–cyclohexyl chloride interaction).[6] The difficulties encountered in applying standard experimental methods to weakly interacting systems have been discussed by several authors.[6,7]

In the preceding paper,[8] conformational analysis of a unimolecular, acyclic model system by nmr spectroscopy was suggested as an approach to the investigation of weak electronic interactions, and evidence for the existence of intramolecular mercury–arene π complexes was described. The present report concerns the application of this technique to a study of mercury coordination with covalent n-electron donors, particularly primary halogen atoms, in organomercury compounds. A related nmr investigation of intramolecular Sn–Br coordination in a 4-bromobutadienyltin compound has recently been communicated.[9] This study has several experimental features in common with the present one, but differs fundamentally in that the development of magnetic nonequivalence in normally isochronous[10] groups is of kinetic rather than thermodynamic origin. Nonetheless, it constitutes an important example of a type of interaction which we suspect is far more prevalent than is commonly realized.

Results

The nmr criteria used to establish the existence of intramolecular mercury–halogen coordination were mostly the same as those described previously for mercury–arene π bonding,[8] except for the absence of anisotropic shielding effects due to aryl substituents and of the chemical shifts of the aromatic protons themselves. Values for the diamagnetic anisotropies of carbon–halogen bonds have been reported,[11] but cannot be regarded as established; in any case, no consistent long-range shielding effects attributable to halogen atoms were detected in the present series of compounds.

As in the previous study,[8] all donor–acceptor pairs were connected through a 2-methyl-2-methoxytrimethylene chain, so that their interaction is represented by eq 1.



(1)

A few compounds bearing other β substituents (including hydrogen) on the trimethylene chain were examined in preliminary work, but found to be less suitable for this type of conformational analysis. Because the donor–acceptor bond energies are in this case similar in magnitude to typical steric conformational energy differences,[12,13] analytical sensitivity is increased by maintaining an approximate "steric balance" in eq 1, *i.e.*, by making all four of the groups attached to the β carbon roughly the same size. However, it is also desirable to maximize the potential methylene group magnetic nonequivalence due to molecular asymmetry at the β carbon, which is very weak if both β substituents are simple alkyl groups. The difficulty in arriving at unequivocal spectral analyses for a whole series of compounds is greatly magnified if the β substituents are methyl and hydrogen: counting mercury–proton coupling, the β-proton signal could be split into as many as 192 first-order lines.

Careful consideration of the nmr spectra of a number of simple β-methoxyalkylmercury compounds[14] has led us to conclude that there is little or no mercury–oxygen valence interaction involving a β-methoxy group, possibly because of the long mercury–carbon bond and acute orbital angles required. The same conclusion has been reached by Brownstein[15] and by Kreevoy and Schaefer.[16] Since this class of compounds is

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(2) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, **85**, 1328 (1963); G. A. Olah, C. U. Pittman, R. Waack, and M. Doran, *ibid.*, **88**, 1488 (1966); G. A. Olah and J. M. Bollinger, *ibid.*, 90, 947 (1968). For a recent review, see G. A. Olah, *Chem. Eng. News*, 45, 77 (March 27, 1967).

(3) P. von R. Schleyer and R. West, *J. Amer. Chem. Soc.*, **81**, 3164 (1959).

(4) R. M. Badger, *J. Chem. Phys.*, **8**, 288 (1940).

(5) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 84, 3221 (1962).

(6) T. D. Epley and R. S. Drago, *ibid.*, **89**, 5770 (1967).

(7) S. D. Ross, *ibid.*, 87, 3032 (1965), and references cited therein; additional references are given in ref 6.

(8) E. F. Kiefer, W. L. Waters, and D. A. Carlson, *J. Amer. Chem. Soc.*, **90**, 5127 (1968).

(9) F. P. Boer, J. J. Flynn, H. H. Freedman, S. V. McKinley, and V. R. Sandel, *ibid.*, **89**, 5068 (1967).

(10) Magnetically equivalent in the chemical shift sense: A. Abragam, "The Principles of Nuclear Magnetism," Oxford, 1961, p 480.

(11) G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

(12) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965.

(13) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, **89**, 1135 (1967).

(14) (a) E. F. Kiefer and W. L. Waters, *ibid.*, 87, 4401 (1965); (b) W. L. Waters, Ph.D. Thesis, University of Hawaii, Honolulu, Hawaii, 1966, and unpublished research in these laboratories.

(15) S. Brownstein, *Discussions Faraday Soc.*, 34, 25 (1962).

(16) M. M. Kreevoy and J. F. Schaefer, *J. Organometal. Chem.*, **6**, 589 (1966).

easily prepared and has desirable physical properties as well as spectral features mentioned above,[14] it is virtually ideal in this case, though with many other Lewis acid acceptors, a β-methoxy group is susceptible to elimination and must be replaced by hydrogen (or deuterium).

Table I shows the changes in methylene group nonequivalence and long-range mercury–proton spin–spin coupling which occur on replacement of mercury or halogen with inert or strongly interacting substituents. As in the preceding paper,[8] nonequivalence is taken as a general indicator of conformational preference, and the relative magnitude of $J_{Hg-C-C-CH_3}$ is considered a specific measure of the extent of chelation (see Figure 1). The value for X = H ($J_{HgCCCH_3} = 22$ Hz) characterizes $K_f = 1$ since the two conformations shown in Figure 1 are then identical. Bulkier but electronically inert groups (X = methyl, *t*-butyl) should lead to a decrease in K_f and thus in J_{HgCCCH_3}, as observed. More basic donor groups (dimethylamino and hydroxyl) lead to the largest values of K_f and J_{HgCCCH_3}. As K_f increases, long-range proton–proton coupling of up to 2.0 Hz[17] develops between hydrogen atoms H_A and H_C, which are *trans,trans* coplanar in the most favorable chelated conformation B (Figure 1). The two N-methyl groups in the dimethylamino compound are magnetically equivalent, showing that intramolecular rotation is still rapid on the nmr time scale even in this strongly chelated compound. In the corresponding palladium compound, the N-methyl groups are magnetically nonequivalent.[18] The OH proton in the hydroxy compound of Table I exchanges only slowly at room temperature in deuteriochloroform, and is spin coupled *stereospecifically* to the α-methylene protons (*J* = 4.0, 8.8 Hz); this phenomenon will be discussed in detail in a separate publication.

Table I. Substituent Effects on Magnetic Nonequivalence and $^{199}Hg-C-C-CH_3$ Coupling in $XCH_2C(CH_3)(OCH_3)CH_2Y$

X	Y	$\Delta\nu_{CH_2X}$[a]	$\Delta\nu_{CH_2Y}$[a]	J_{HgCCCH_3}, Hz
Cl	HgCl	16.5	<4	29.5
Br	HgCl	19.1	13.6	32
OH	HgI	42.5	32.1	*c*
NMe_2	HgCl	65[b]	69[b]	46
H	HgCl	...	...	22
CH_3	HgCl	<4[b]	<4[b]	20
CMe_3	HgCl	9.0[b]	12.2[b]	16
Br	Br	<5[b]	...	...

[a] Chemical shift between methylene protons in hertz at 100 MHz. [b] Calculated from the 60-MHz spectrum. [c] Hg satellites too broad to be detected.

If these criteria are valid, it can be seen (Table I) that γ-chlorine and -bromine atoms are coordinated, though rather weakly, with mercury. Bromine is the stronger donor, as might be expected. The corresponding iodomethylene compounds could not be prepared: treatment of methallyl iodide with mercuric acetate under a variety of conditions resulted in rapid elimination of mercuric iodide. The methallyl bromide and chloride adducts decompose in apparently the same way, but more slowly. The nature of this reaction is currently under investigation.

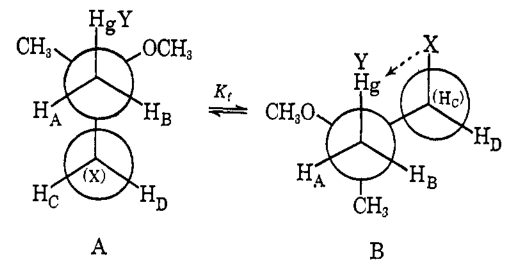

Figure 1. Angular relationships in the sterically and electronically preferred conformations of 3-halo-2-methyl-2-methoxypropylmercury compounds. Long-range Hg-C-C-CH_3 and H_A-C-C-C-H_C coupling is at a maximum in the chelated conformation B.

Table II illustrates the ligand dependence of mercury coordination with primary chlorine and bromine atoms. Mercury–halogen interaction appears to be stronger in halomercuri than in cyanomercuri compounds, contrary to the order observed in the mercury–arene π complexes[8] and in the formation constants of methylmercury with the corresponding anions.[19] Since unsymmetrical covalent mercury compounds are not particularly susceptible to ligand disproportionation,[20] the cause of this apparent anomaly is unknown. No intramolecular exchange or intermolecular disproportionation of mercury and carbon ligands was observed in any of the present compounds.

Table II. Ligand Effects on Mercury–Halogen Coordination in $XCH_2C(CH_3)(OCH_3)CH_2HgY$

Y	$\Delta\nu_{CH_2X}$, Hz	$\Delta\nu_{CH_2Hg}$, Hz	J_{HgCCCH_3}, Hz	J_{HgCH}, Hz
		A. X = Cl		
OAc	8.7	<3	25	212
Cl	16.5	<4	29	200
Br	17.4	<4	29.5	192
I	17.2	7.4	...	...
CN	21.3	15.6	25	178
		B. X = Br		
OAc	10.8	<4	27	211
Cl	19.1	13.6	32	201
I	19.4	17.2	...	...

Data on Hg-C-H coupling are included in Tables II and III to show that ligand and solvent effects on Hg-C-C-CH_3 coupling are indeed due to conformational changes. Singh[21] examined the effect of solvent polarity and concentration on α and γ coupling in neopentylmercuric chloride and bromide and dineopentylmercury and found that the ratio $J_\alpha/J_\gamma = 15.5$ remained fairly constant for all three compounds. Both types of coupling increased with the degree of ionic character of the mercury–ligand bond (Hg-Cl > Hg-Br > Hg-C) and with increasing solvent polarity (for the two unsymmetrical, dipolar compounds only; J_α and J_γ were both solvent independent in dineopentylmercury). The same ligand polarity effect on J_α (ClO_4 > OAc > Cl > Br > I > CN ≫ R) has been

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(17) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 5.

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

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

(20) N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, London, 1950, pp 308, 327 ff.

(21) G. Singh, *J. Organometal. Chem.*, **5**, 577 (1966).

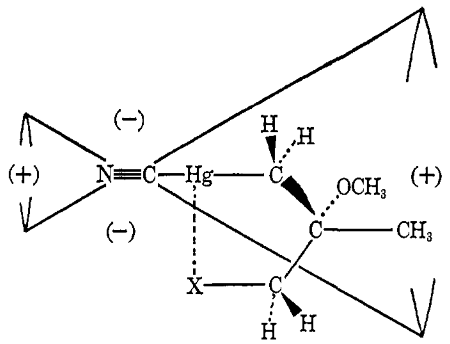

Figure 2. Shielding (+) and deshielding (−) regions due to magnetic anisotropy of a cyano group.

noted elsewhere,[22] and is ascribed to changes in the fractional s-orbital character of the remaining mercury–carbon bond. Brownstein[15] and we[14] have noted that J_γ seems to be fairly ligand independent in simple mono-(β-methoxyalkyl)mercury derivatives, however.

Table III. Solvent Effects on Magnetic Nonequivalence and ^{199}Hg–^{1}H Coupling in $XCH_2C(CH_3)(OCH_3)CH_2HgCl$

Solvent ($\epsilon^{25°}$)	$\Delta\nu_{CH_2X}$, Hz	$\Delta\nu_{CH_2Hg}$, Hz	J_{HgCCCH_3}, Hz	J_{HgCH},[a] Hz
		A. X = Cl		
PhNO$_2$ (34.8)	21.5	9.3	31.5	(208)
C$_6$H$_6$ (2.3)	20.9	<3	27.5	206
CCl$_4$ (2.2)	16.5	<4	29.5	200
(CD$_3$)$_2$CO (20.7)	13.2	<3	27	214
Pyridine (12.3)	<2	<3	20	(229)
		B. X = Br		
CCl$_3$CN	25.3	21.2	36	(201)
CDCl$_3$ (4.8)	25.2	19.1	36	201
PhNO$_2$ (34.8)	21.9	15.6	35	(203)
CCl$_4$ (2.2)	19.1	13.6	32	201
(CD$_3$)$_2$CO (20.7)	15.5	12.9	23	(187)
Pyridine (12.3)	<2	<3	20	(225)

[a] None of the ^{199}Hg–^{1}H α-coupling assignments were verified. Those in parentheses should be considered tentative.

The data of Table IV verify that K_f increases slightly on dilution in a nonpolar solvent, as expected for a weak interaction which has unimolecular and bimolecular components in equilibrium. Neither the chemical shifts nor the mercury-proton coupling constants of the neopentylmercury compounds examined by Singh[21] showed any variation with concentration over the more limited range investigated. The temperature dependence of chemical shifts and coupling constants shown in Table V establishes the existence of a conformational energy difference[12,16] and allows a rough calculation of its magnitude, based on assumed $\Delta\nu_{CH_2}$ and J values for each individual conformer (see below).

Table IV. Concentration Dependence of Magnetic Nonequivalence and ^{199}Hg–^{1}H Coupling in $BrCH_2C(CH_3)(OCH_3)CH_2HgCl$[a]

Concn, %	$\Delta\nu_{CH_2Br}$, Hz	$\Delta\nu_{CH_2Hg}$, Hz	J_{HgCCCH_3}, Hz
1.0	26.3	19.9	36.0
2.5	25.6	19.4	35.5
5.0	25.1	19.4	36.0
10.0	24.7	19.4	35.5
20.0	23.5	18.1	35.0

[a] In CDCl$_3$.

Table V. Temperature Dependence of Magnetic Nonequivalence and ^{199}Hg–^{1}H Coupling in $BrCH_2C(CH_3)(OCH_3)CH_2HgCl$[a]

Temp, °C	$\Delta\nu_{CH_2Br}$, Hz	$\Delta\nu_{CH_2Hg}$, Hz	J_{HgCCCH_3}, Hz
42.5	25.2	19.4	36.0
9.0	28.0	22.0	37.5
−32.5	34.2	28.3	41.0

[a] In CDCl$_3$.

In the previous study of mercury–arene coordination,[8] use was made of the strongly anisotropic shielding effect of aryl substituents as an additional conformational probe. Over-all chemical shift differences among the present series of compounds were much smaller, and no clear-cut trends in δ values which might be ascribed to conformational effects were discernible. A small (and quite possibly fortuitous) chemical shift effect was noted for cyanomercury derivatives, however (Table VI), which is consistent with the long-range shielding behavior expected for the cyano group[23] as shown in Figure 2.

Table VI. Ligand Effects on Chemical Shifts in $ClCH_2C(CH_3)(OCH_3)CH_2HgX$

X	τ_{CH_2Cl}	τ_{OCH_3}	τ_{CH_2Hg}	τ_{CH_3}
OCOCH$_3$	6.51	6.74	7.87	8.63
Cl	6.51	6.75	7.92	8.64
Br	6.51	6.75	7.89	8.63
I	6.51	6.76	7.89	8.64
CN	6.49	6.79	8.19	8.66

Perhaps the most convincing demonstration of the authenticity of methylene group nonequivalence as a conformational probe in this model is the spectral change which occurs upon addition of sodium iodide to a solution of 3-bromo-2-methyl-2-methoxypropylmercuric iodide in acetone-d_6. The results of this "conformational titration" are shown in Figure 3 and tabulated in Table VII. Free iodide ion should readily displace covalent iodine from coordination with mercury,[19] and 0.5 mol of added iodide results in equal quantities of chelated (RHgI) and open-chain ($RHgI_2^-$) conformers. With rapid iodide exchange, the nmr spectrum resembles that of a single species for which $K_f \approx 1.0$, and the methylene quartets collapse to singlets. Addition of more iodide gives rise ultimately to $RHgI_3^{2-}$ in which both steric and electronic factors should drive the conformational equilibrium (eq 1) strongly to the left, and magnetic nonequivalence re-

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(22) J. V. Hatton, W. G. Schneider, and W. Siebrand, *J. Chem. Phys.*, **39**, 1330 (1963).

(23) J. A. Pople, *ibid.*, **37**, 53 (1962); G. S. Reddy and J. H. Goldstein, *ibid.*, **39**, 3509 (1963); A. D. Cross and I. T. Harrison, *J. Amer. Chem. Soc.*, **85**, 3223 (1963).

Table VII. Effect of Added Sodium Iodide on Magnetic Nonequivalence in $BrCH_2C(CH_3)(OCH_3)CH_2HgI$

NaI, mol	$\Delta\nu_{CH_2Br}$,[a] Hz	$\Delta\nu_{CH_2Hg}$,[a] Hz
0.0	±13.0	±12.6
0.5	<2	<3
1.0	∓4.8	<3
2.0	∓8.7	∓4–6[b]

[a] Relative signs of coupling constants were not verified (see text).
[b] Methylene signal obscured by acetone-d_5 proton multiplet.

turns. The available data do not permit individual chemical shift assignments for each methylene proton in $RHgI_3^{2-}$, so it cannot be verified that $\Delta\nu_{CH_2}$ changes sign[24] as required by this interpretation (*cf.* Table VII); however, it is perhaps significant that stereospecific long-range proton-proton coupling is visible in the spectrum of RHgI but absent in that of the iodide complex (*cf.* Figure 1).

Discussion

A quantitative assessment of donor-acceptor bond strengths in these and other systems will be the subject of a later publication; however, it seems worthwhile at this point to obtain an estimate of the mercury-halogen coordination enthalpy. As mentioned above, the temperature dependence of $\Delta\nu_{CH_2}$ or J_{HgCCCH_3} can be used for this purpose if appropriate values for at least one of the limiting conformations are at hand. Assuming there are no important methylene-substituent effects on mercury-methyl coupling other than those resulting from conformational changes, the value of J_{HgCCCH_3} from Table I for X = H (22 Hz) can be equated with $\Delta H = 0$, since the two conformations of eq 1 and Figure 1 are identical in this case. Ethyl is probably a somewhat better choice than methyl as a steric model for the bromomethylene group, however,[12,13] so J_{HgCCCH_3} = 20 Hz (from X = CH_3, Table I) is assumed for 3-bromo-2-methyl-2-methoxypropylmercuric chloride (X = Br) in the absence of mercury-halogen coordination, *i.e.*, for the mixture of conformers which would result from purely steric interactions. This assumption is strongly supported by the fact that J = 20 Hz for the bromo compound in pyridine, a solvent which should effectively quench intramolecular Hg-Br coordination[8] (*cf.* Table III). The data of Table V then produce the best fit in the van't Hoff equation when J_{HgCCCH_3} = 60 Hz is assumed for the pure chelate conformer, in which case ΔH = 1.1 kcal/mol for the mercury-bromine interaction. The same treatment of temperature-dependent chemical shift data for the bromomethylene group (Table V) gives ΔH = 1.04 kcal/mol, assuming $\Delta\nu_{CH_2Br}$ = 0 Hz for the limiting steric conformer.[8] In this case, the best value obtained for the limiting chelate conformer is 65 Hz, in striking agreement with the value of $\Delta\nu_{CH_2X}$ in the strongly chelated dimethylamino derivative (Table I). Repeating the calculation with the $\Delta\nu_{CH_2Hg}$ low-temperature data gives $\Delta\nu_{chelate}$ = 51 Hz and ΔH = 1.27 kcal/mol, which is still in satisfactory agreement considering the large number of assumptions and the small number of experimental points involved.

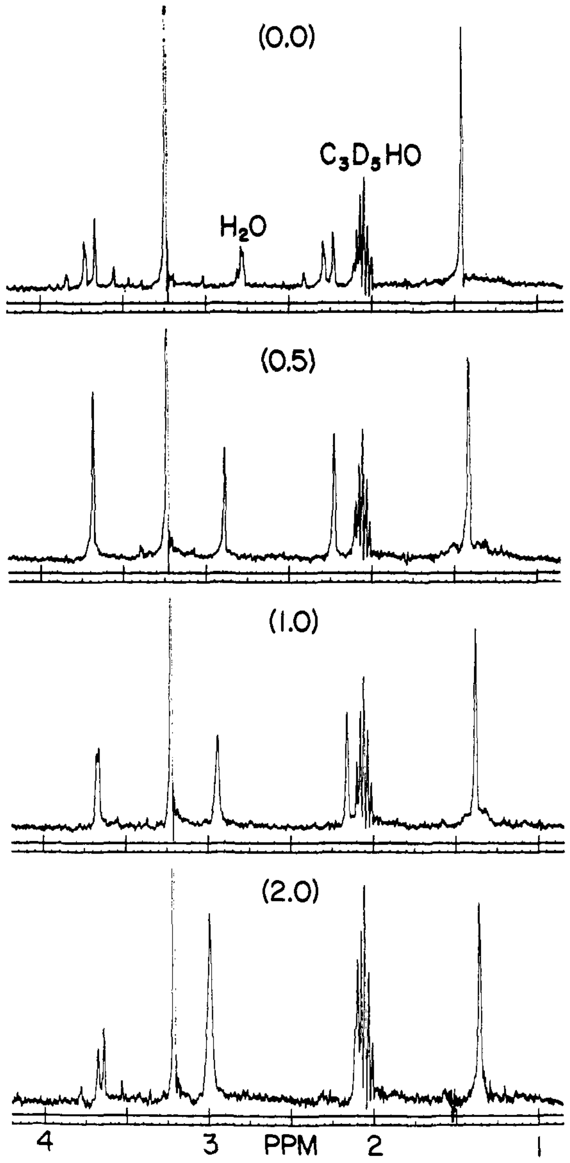

Figure 3. The effect of added NaI (mole equivalents indicated in parentheses) on proton chemical shift nonequivalence of CH_2Br (3.70 ppm) and CH_2Hg (2.25 ppm) in $BrCH_2C(CH_3)(OCH_3)$-CH_2HgI in acetone-d_6, 100 MHz.

The value of 60 Hz obtained above for the maximum coupling of mercury with a *trans*-β-methyl group, when compared with the value of 22 Hz for the β-methyl groups in 2-methyl-2-methoxypropylmercuric chloride (Table I) and in 3-methyl-3-methoxy-2-butylmercuric chloride,[14] suggests the interesting possibility that J_{gauche} may be negative relative to J_{trans}. If 22 Hz represents the average of one *gauche* and one *trans* coupling, then J_{gauche} = −16 Hz. In *trans*-2-methyl- and *trans*-1,2-dimethyl-2-methoxycyclohexylmercuric chloride, which have *gauche*-Hg-C-C-CH_3 geometry, $|J_{HgCCCH_3}|$ = 7 Hz.[14b] 2,3,3-Trimethyl-2-methoxybutylmercuric chloride, in which the bulky *t*-butyl group should force the β-methyl substituent to be *gauche* to mercury, shows $|J_{HgCCCH_3}|$ = 26 Hz,[14] a value which is difficult to explain if J_{gauche} and J_{trans} have the same sign. A change in the sign of J_{HgCCCH_3} with di-

(24) An authentic "crossover" of methylene proton chemical shifts has been noted for styrene dibromide when the solvent is changed from carbon tetrachloride to acetone: M. Buza and E. I. Snyder, *J. Amer. Chem. Soc.*, 88, 1161 (1966). The relatively small solvent shift observed ($\Delta\Delta\nu < 0.1$ ppm) is consistent with a change in relative conformer populations indicated by the reported solvent dependence of vicinal coupling constants: $|J_{AX} - J_{BX}|$ decreases by 1.3 Hz, corresponding to a conformational $\Delta\Delta E$ of about 0.3 kcal/mol.[13]

hedral angle might also explain the fact that the more conformationally mobile propyl- and 2-butylmercury derivatives show no β-methyl coupling with mercury at all.[14,15]

The mercury–chlorine bond is clearly weaker than that with bromine, yet it is still well above the limit of detectability. Although a number of implications of the results obtained for these particular donor–acceptor interactions could be cited, it seems appropriate to defer such discussion until more quantitative data are available and the experimental model has been subjected to broader scrutiny. In addition to the inherent limitations mentioned previously,[8] the model is further restricted by the somewhat contradictory requirements of minimum steric imbalance and maximum magnetic anisotropy about the central asymmetric carbon atom, as discussed above. To the extent that either of these structural features must be sacrificed for chemical stability, etc., the sensitivity of the method drops rather sharply, a consequence of the relatively high noise level which characterizes the present state of chemical shift theory and conformational analysis. Another problem is that many interesting systems, particularly organometallics, are unpreparable or insoluble in the absence of strong solvation, which blocks the potential acceptor site toward weak intramolecular donors (*cf.* Table III).

None of the above considerations is of major consequence in ordinary covalent organic compounds, however, and the model may prove to have its greatest utility in studying ground-state interactions between purely organic functional groups, such as hydrophobic bonding, transient π–π complexes, and dipole–dipole attraction. At the very least, such studies should result in intensive evaluation and probably some refinement of existing data on magnetic anisotropies and steric conformational energies in acyclic systems.

Experimental Section

Materials. Acetoxymercuri compounds were prepared by oxymercuration of the appropriate 3-substituted 2-methylpropene with reagent grade mercuric acetate in anhydrous methanol as described previously,[25] on a 0.05–0.1-mol scale. These were converted to the chloromercuri, bromomercuri, and iodomercuri derivatives by treatment with a *ca.* threefold excess of the appropriate sodium or potassium halide in water, and recrystallized if necessary from benzene–ligroin. Since the cyanomercuri derivative from methallyl bromide was quite soluble in the presence of excess cyanide ion, equimolar amounts of the reagents were used in this case. The iodomercuri derivatives and all of the methallyl bromide adducts decomposed fairly rapidly unless stored at 0° in the dark. All of the compounds used in this work are adequately characterized by their nmr spectra.

Table VIII. Preparative Data for Methallyl Halide Oxymercuration Products, $XCH_2C(CH_3)(OCH_3)CH_2HgY$

X	Y	Mp, °C	Yield, %
Cl	OAc	65–66	91
Cl	Cl	38–39	92
Cl	Br	(Oil)	[a]
Cl	I	46–47	96
Cl	CN	56–57	99
Br	OAc	57.5–58.5	94
Br	Cl	65–66.5	89
Br	I	35–35.5	92
Br	CN	85–86	72

[a] Not calculated.

Spectra. Nuclear magnetic resonance spectra were measured at 100 MHz using a Varian HA-100 spectrometer system in the frequency sweep mode, with tetramethylsilane as internal lock. Sweep widths were calibrated periodically with the digital frequency counter. All spectra data reported herein were obtained using 5% solutions of sample in carbon tetrachloride at an ambient probe temperature of 42.5°, unless otherwise noted. Subambient temperatures were measured by the standard methanol calibration, and are approximately ±3°. The estimated precision of measured chemical shifts and coupling constants is ±0.5 Hz. For the experiments involving added iodide ion, a measured volume of 0.20 *M* sodium iodide in acetone-d_6 was added from a 1-ml syringe to 0.5 ml of a 0.10 *M* (5 wt %) solution of 3-bromo-2-methyl-2-methoxypropylmercuric iodide in the same solvent in a standard nmr tube. The spectra of Figure 3 were all recorded for a single run. The original neutral adduct was regenerated from the iodide complex by pouring the sample into a large volume of water.

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