

## VICINAL $^1\text{H}$ - $^{199}\text{Hg}$ COUPLING CONSTANTS

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### INTRODUCTION

The measurement and interpretation of  $^1\text{H}$ - $^1\text{H}$  coupling constants in nuclear magnetic resonance (NMR) spectroscopy has contributed substantially to the known stereochemistry of hydrocarbons, carbohydrates and related substances<sup>1</sup>. (References to experimental work are given by Karplus<sup>1</sup>.) To a substantial degree this information has followed on the discovery of a systematic relation between the coupling constant for protons on vicinal carbon atoms,  $J(\text{H-H})_{\text{vic}}$ , and their dihedral angle<sup>1,2</sup>. The present paper suggests the existence of a systematic relation between dihedral angle,  $\tau$ , and the coupling constant for  $^1\text{H}$  and  $^{199}\text{Hg}$  on vicinal carbons,  $J(\text{H-Hg})_{\text{vic}}$ .

The suggested new relation supports a previous finding<sup>3</sup> that halo mercury groups attached to a cyclohexane ring have little or no preference for equatorial *vs.* axial positions. It further suggests that there is no preference for a *trans* as opposed to a *gauche* relation between oxygen functions and halomercury groups on adjacent carbon atoms. The reason for this is probably that its long covalent bond to carbon (2.2 Å)<sup>4</sup> effectively removes the  $\text{HgX}$  group from the vicinity of potential non-bonded interactions.

### RESULTS

Proton magnetic resonance spectra of the compounds shown in Table I all showed recognizable  $^{199}\text{Hg}$  satellites in addition to proton-proton coupling. Table I gives the various  $J(\text{H-Hg})$  obtained. Suitable spectra were obtained from saturated or supersaturated solutions in deuteriochloroform or, in one case, the neat liquid. The NMR spectrum of (I) has been previously reported<sup>5</sup> and the present results generally resemble the older ones. However, the present  $^{199}\text{Hg}$  coupling constants for (I), reported in Table I, are 10–15 c/sec smaller than those previously reported. The discrepancy is beyond the reported limits of uncertainty. It is certainly well outside the uncertainty in the present results.

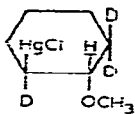
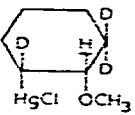
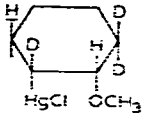
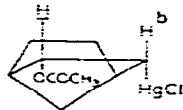
Typical spectra of (II) and (III) are shown in Figs. 1 and 2, and discussed in adjacent text. The spectrum of (II) was actually obtained on a mixture of (II) and (IIa), and that of (III) on a mixture with (IIIa), but neither of the "a" compounds have any unique absorption in the region of the peak due to  $-\text{CHOCH}_3-$  or its satellites. The spectrum of (IV) was very complicated and most of it was not analyzed, but the

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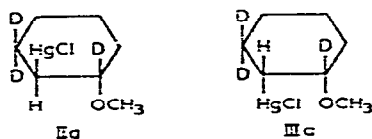
doublet due to the proton of interest was well separated from the rest of the spectrum, about 140 c/sec upfield from the residual  $\text{CHCl}_3$  in the solvent at 56.4 Mc/sec. The doublet, and both of its satellites, could be identified by inspection. The spectrum of (V), apart from the ethyl groups and the  $^{199}\text{Hg}$  satellites, could be completely analyzed

TABLE I  
 $J(\text{H-Hg})$  in  $\text{CDCl}_3$  AT ROOM TEMPERATURE

| Compound <sup>a</sup>                                                               | Designation<br>in text | $J(\text{H-Hg})^{\text{a,d}}$<br>(c/sec) |
|-------------------------------------------------------------------------------------|------------------------|------------------------------------------|
| $\text{CH}_3\text{OCH}_2\text{CH}_2\text{HgCl}$                                     | (I)                    | 231.5                                    |
| $\text{CH}_3\text{OCH}_2\text{CH}_2\text{HgCl}$                                     | (I)                    | 216.4                                    |
|    | (II)                   | 99                                       |
|    | (III)                  | 425                                      |
|   | (III)                  | 517                                      |
|  | (IV)                   | 93.2                                     |
| $(\text{C}_2\text{H}_5\text{O})_2\text{CHCH}_2\text{HgCl}$                          | (V)                    | 236 <sup>c</sup>                         |
| $(\text{C}_2\text{H}_5\text{O})_2\text{CHCH}_2\text{HgCl}$                          | (V)                    | 223 <sup>c</sup>                         |

<sup>a</sup> The pertinent proton is underlined in each structure. <sup>b</sup> Compound kindly furnished by Professor T. G. TRAYLOR, University of California at San Diego. <sup>c</sup> Measured in the neat liquid. <sup>d</sup> At 33°.

as that of an  $\text{A}_2\text{X}$  system. After several minor peaks had been shown, by comparison of 60 Mc/sec and 100 Mc/sec spectra, to be due to  $\text{ClHgCH}_2\text{CHO}$ , present as an impurity, the  $^{199}\text{Hg}$  satellites could be identified by inspection. A typical spectrum is shown in fig. 3.



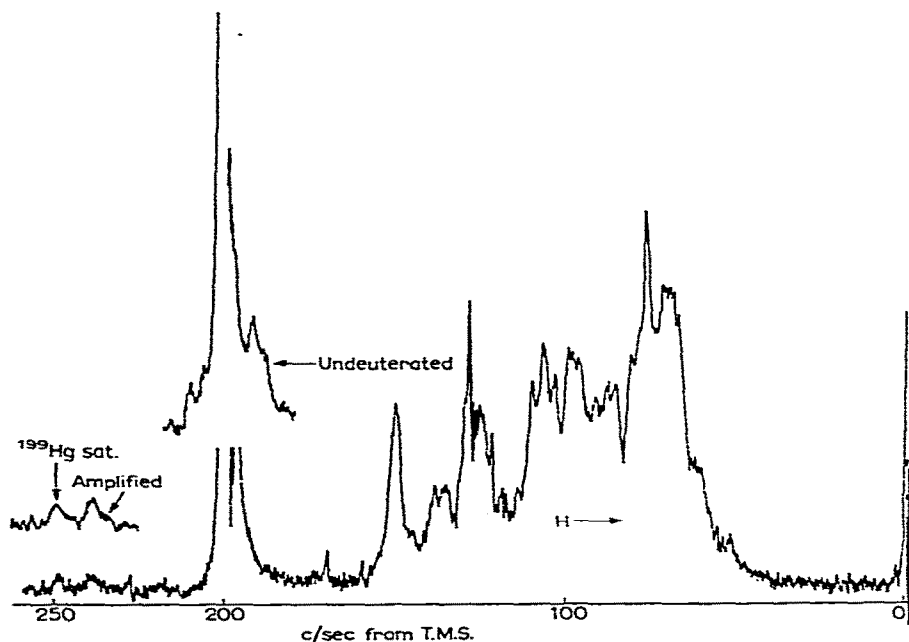


Fig. 1. NMR spectrum of a 1:1 mixture of (II) and (IIa) at 60 Mc/sec in  $\text{CDCl}_3$ .

For all compounds except (I), values of  $J(\text{H-Hg})$  were obtained by the usual measurements on calibrated spectra. They are all uncertain by several c/sec. For (I) the side band superposition technique was used and these  $J(\text{H-Hg})$  are thought to be uncertain by no more than 1.0 c/sec.

In addition to the  $J(\text{H-Hg})$  values at room temperature, a number were determined by the same techniques at elevated temperatures. These are shown in Table 2.

The sharp line at the origin of the spectrum in Fig. 1 is tetramethylsilane (TMS). The broad group of lines ranging from 50 to 160 c/sec downfield from TMS are due to

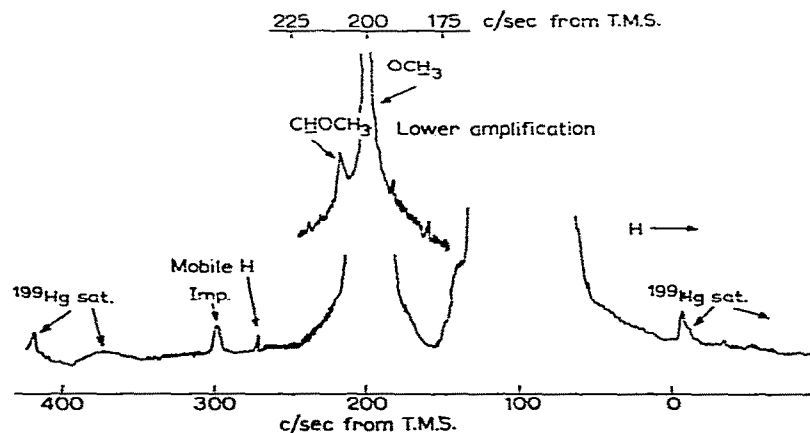


Fig. 2. NMR spectra of a 1:1 mixture of (III) and (IIIa) at 56.4 Mc/sec in  $\text{CDCl}_3$ .

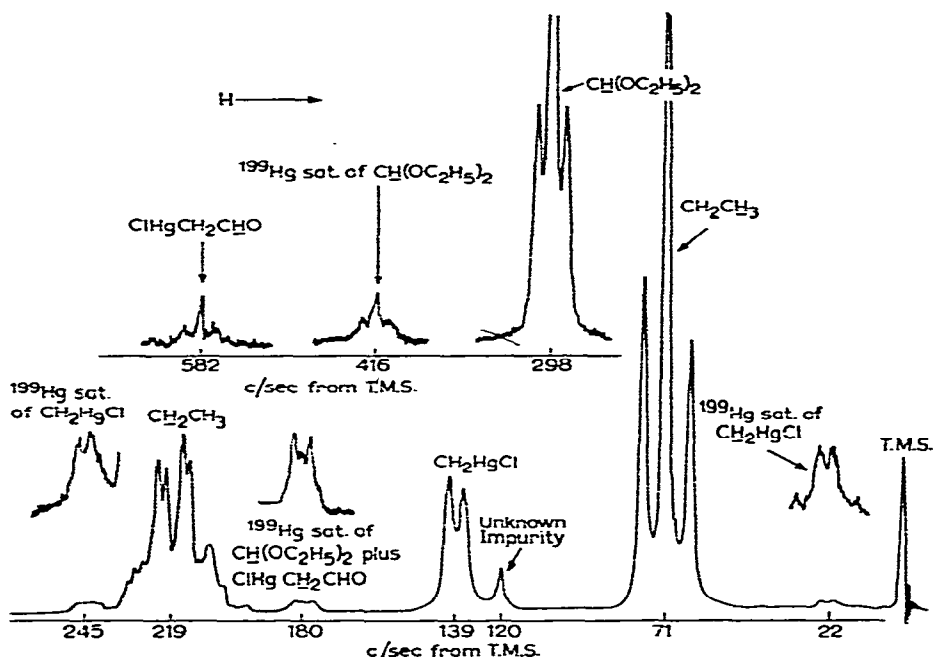


Fig. 3. NMR spectrum of (V) as a neat liquid at 60 Mc/sec.

the methylene protons and the  $-\text{CHHgCl}-$  proton of (IIa). The sharp peak 200 c/sec downfield from TMS is due to the methoxyl protons, superimposed on the methine proton *gem* to the methoxyl group. This superposition is established by comparison with the undeuterated analogue of (II), by comparison of the intensity ratio of the sharp peak to the rest of the spectrum [obs., 1.79; calcd. for a 1:1 mixture of (II) and (IIa), 1.86] and by the absence of an alternative peak of appropriate chemical shift. Of the two peaks of appropriate intensity to be  $^{199}\text{Hg}$  satellites of the  $-\text{CHOCH}_3-$  peak the one at higher field cannot be correct because of the absence of a similar peak symmetrically placed about the main peak. Since no other peaks appear at lower field there is no

TABLE 2

$J(\text{H}-\text{Hg})$  VALUES AT VARIOUS TEMPERATURES

| Compound | $T$<br>( $^{\circ}\text{C}$ ) | $J(\text{H}-\text{Hg})_{\text{gem}}$<br>(c/sec) | $J(\text{H}-\text{Hg})_{\text{vic}}$<br>(c/sec) |
|----------|-------------------------------|-------------------------------------------------|-------------------------------------------------|
| (I)      | 33                            | 216.4                                           | 231.3                                           |
| (I)      | 58                            | 215.4                                           | 232.8                                           |
| (I)      | 95                            | 215.0                                           | 232.2                                           |
| (I)      | 145                           | 214.4                                           | 232.6                                           |
| (II)     | 33                            |                                                 | 99                                              |
| (II)     | 100                           |                                                 | 99                                              |
| (III)    | 33                            |                                                 | 425                                             |
| (III)    | 95                            |                                                 | 409                                             |
| (III)    | 140                           |                                                 | 395                                             |

alternative to the assignment shown.  $J(\text{H-Hg})$  was obtained by doubling the separation between the main peak and the satellite.

The spectrum in Fig. 2 shows no TMS, because one of the  $^{199}\text{Hg}$  satellites was very nearly superimposed on the TMS peak. The calibration and the chemical shifts of the sharp, intense peaks were obtained from a low intensity spectrum, with TMS added. The peak due to residual  $\text{CHCl}_3$  was observed at an appropriate position (off scale on the present figure). The broad absorption between 50 and 150 c/sec from TMS must be due to the methylene groups. The methoxyl peak and the  $-\text{CHOCH}_3-$  peak are assigned from their chemical shifts<sup>5</sup>, their intensities, and their sharpness. The assignment of the  $^{199}\text{Hg}$  satellites centered about the  $\text{CHOCH}_3$  peak is straightforward after it is noted that the unknown impurity peak disappears on heating, and the mobile hydrogen peak is both enhanced and shifted by the addition of a drop of methanol.  $J(\text{H-Hg})_{\text{vic}}$  was obtained by measuring from satellite to satellite. Another pair of  $^{199}\text{Hg}$  satellites is also visible. These are much broader than those centered about the  $-\text{CHOCH}_3-$  peak and are centered about a point in the featureless methylene band. One of them is visible at 372 c/sec from TMS and the other is just off scale, at -145 c/sec from TMS. They give a  $J(\text{H-Hg})$  of 517 c/sec and are assigned to the methylene proton *trans* to the  $\text{HgCl}$  group for reasons that will become apparent.

The assignment of the major bands in Fig. 3 is obvious from their multiplicity and intensity. The assignment of  $^{199}\text{Hg}$  satellites becomes straightforward when it is noted that the triplet at 416 c/sec from TMS and that at 298 c/sec from TMS retain that separation at 100 Mc/sec, while the separation between the 582 c/sec band and that at 298 c/sec increases to 465 c/sec. The small peak at 120 c/sec from TMS is found at 200 c/sec from TMS at 100 Mc, and is, therefore, the parent peak of an impurity. The spectrum at 100 Mc/sec shows no further peaks of sufficient intensity to be  $^{199}\text{Hg}$  satellites of the parent compound.

#### DISCUSSION

The present  $J(\text{H-Hg})_{\text{vic}}$  values can be rationalized with the aid of the following hypotheses.

(1) Values of  $J(\text{H-Hg})_{\text{vic}}$  are generally around 100 c/sec except when the dihedral angle,  $\varphi$ , defined by the C, C, H plane and the C, C, Hg plane, is close to  $180^\circ$ . In the interval between  $120^\circ$  and  $180^\circ$  it rises to around 600 c/sec.

(2) In its lateral interactions with fairly small *vicinal* atoms and groups, the chloromercuri group behaves approximately like a hydrogen atom.

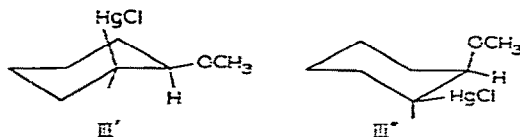
A value of  $J(\text{H-Hg})_{\text{vic}}$  for  $\varphi$ ,  $\sim 120^\circ$ , is obtained directly from compound (IV), which is rigid and in which  $\varphi$  is constrained to something near that value. It is 93 c/sec. That for  $60^\circ$  is obtained from compound (II), in which  $\varphi$  is about  $60^\circ$  in either of the chair conformers. It is 99 c/sec. In addition Traylor and Factor<sup>6</sup> have observed four  $J(\text{H-Hg})$  close to 100 c/sec with di-*exo*-norbornene derivatives in which  $\varphi$  is constrained to a value close to  $120^\circ$ , and one  $J(\text{H-Hg})_{\text{vic}}$  close to 100 c/sec with a norbornene derivative in which  $\varphi$  is constrained to a value close to  $0^\circ$ . The value of  $J(\text{H-Hg})_{\text{vic}}$  for  $\varphi$ ,  $\sim 180^\circ$ ,  $\sim 600$  c/sec is the round number which best reproduces the rest of the results, including the temperature dependences. It is clear that the quantitative significance of these numbers is limited, and the exact function relating dihedral angle and  $J(\text{H-Hg})_{\text{vic}}$  is somewhat uncertain. Nevertheless only a pattern similar to that hypothesized will rationalize all the results.

The second hypothesis was suggested by the work of Jensen and Gale<sup>3</sup>. It is required by the observation that (I), (V), and ethylmercuric chloride have about the same values for  $J(\text{H-Hg})_{\text{rte}}$  if inductive effects on the coupling constant are assumed to be small. The value for ethylmercuric chloride is 296 c/sec<sup>7</sup>. Using hypotheses (1) and (2), a value of 267 c/sec for  $J(\text{H-Hg})_{\text{rte}}$  is predicted in all three cases. This is in quite acceptable agreement with the observed values, 232, 236, and 296 c/sec. If there were a strong preference for a *gauche* O-Hg orientation, the predicted value for (I) would be 350 c/sec, which cannot be absolutely ruled out, but the predicted value for (V) would be 600 c/sec, which is clearly at variance with experiment. If there were a strong preference for a *trans* O-Hg orientation, the predicted value for (I) and (V) would both be 100 c/sec. The disagreement between this value and experiment becomes particularly unattractive when it is recalled that only  $J(\text{H-Hg})_{\text{rte}}$  for  $\varphi$ , 60°, need be used to make this prediction, and the latter rests very firmly on a substance of known  $\varphi$ .

The observation that  $J(\text{H-Hg})_{\text{rte}}$  for (I) is temperature independent within very narrow limits of uncertainty puts severe restraints on the allowed  $\Delta H^\circ$  for *trans*, *gauche* isomerization. The value can either be very small, producing a statistical distribution in all cases, or it can be very large, producing a single "frozen" conformation. In the latter case the preference for the O-Hg *gauche* orientation would have to be  $> 3.5$  kcal·mole<sup>-1</sup> to avoid producing a 2 c/sec change in  $J(\text{H-Hg})_{\text{rte}}$  on changing the temperature from 33° to 145°. If the preference were for the *trans* conformer it must be  $> 4.5$  kcal·mole<sup>-1</sup> to avoid a 2 c/sec change over that temperature range. If an approximately statistical distribution is postulated neither conformer can be favored by more than  $\sim 0.1$  kcal·mole<sup>-1</sup>. These conclusions are reached by using eqn. (1) to obtain the ratio of *gauche* to *trans* conformers. This assumes that there is no

$$(g)/(t) = 2\exp(-\Delta H^\circ/RT) \quad (1)$$

entropy difference between the conformers other than the statistical factor of 2. The standard enthalpy of the *trans*-to-*gauche* conversion is  $\Delta H^\circ$ . The *gauche*-to-*trans* ratio,  $(g)/(t)$ , is readily converted to a coupling constant by use of hypothesis (1). The numerical limits of permissible  $\Delta H^\circ$  values, of course, depend on that hypothesis, but the general conclusion that  $\Delta H^\circ$  must be either very small or quite large follows from any assignment in which *gauche* and *trans*  $J(\text{H-Hg})_{\text{rte}}$  have quite different values. Since a large preference for one or the other conformer has already been excluded by comparison of  $J(\text{H-Hg})_{\text{rte}}$  for (I), (V), and ethylmercuric chloride only the small value of  $\Delta H^\circ$  fits all the observations.



The temperature variation of  $J(\text{H-Hg})_{\text{rte}}$  for (III) is satisfactorily predicted by hypotheses (1) and (2). For the conversion of (III') to (III'')  $\Delta H^\circ$  should be just the equatorial, axial isomerization energy of methoxycyclohexane, 0.6 kcal·mole<sup>-1</sup>

(ref. 8). Using eqn. 2 to evaluate the population distribution and hypothesis (1) for the required coupling constants of pure conformers,  $J(\text{H-Hg})_{vic}$  values of 462, 447,

$$(\text{III}')/(\text{III}') = \exp(-300/T) \quad (2)$$

and 432 c/sec are predicted at 33°, 95°, and 140°, respectively. Both in absolute value and in temperature variation these are in very acceptable agreement with the experimental values of 425, 409, and 395 c/sec. The agreement of the absolute values cannot be given too much weight, because (III) was one of the compounds used in assigning  $J(\text{H-Hg})_{vic}$  for  $\varphi$ , 180°. The excellent agreement in the temperature variation supports hypothesis (2) but does not require it, as values of  $\Delta H^\circ$  from 0.6 to 1.5 kcal·mole<sup>-1</sup> can produce agreement about as good, particularly if some variation in assigned values of  $J(\text{H-Hg})_{vic}$  is also allowed. No temperature variation is predicted for (II), and it shows none.

In an earlier paper it was pointed out that the infrared spectrum of liquid 2-methoxyethylmercuric iodide is very similar to that of the solid<sup>9</sup>. Since the solid is probably conformationally homogeneous, with the *trans* O-Hg orientation preferred, it was concluded that this was true of the liquid, as well. Later results on rates and equilibria were incompatible with a preference for a *trans* O-Hg orientation in solution but compatible with a preferred *gauche* orientation<sup>10</sup>. The latter conclusion was adopted because of the previous infrared results, but this is now shown to be incorrect. It now seems that either the solid is not conformationally homogeneous, or (more likely) that the similarity between solid state and liquid state spectra is fortuitous. The kinetic and equilibrium studies<sup>10</sup> are perfectly compatible with hypothesis (2).

Brownstein<sup>5</sup>, on the basis of  $^1\text{H}$ - $^{199}\text{Hg}$  coupling constants, has concluded that  $\text{OCH}_3$  groups and  $\text{HgX}$  groups on vicinal carbons have little or no preference for *trans* or *gauche* orientations. However, from the fact that  $J(\text{H-Hg})_{vic}$  for 2-methoxypropylmercuric compounds are *larger* by 50–80 c/sec than those for the comparable 2-methoxyethylmercuric compounds he concluded that  $J(\text{H-Hg})_{vic}$  was *larger* for *gauche* than for *trans* orientations, and that the methyl group and the  $\text{HgX}$  group preferred a *trans* orientation. Both of these last two conclusions now seem unlikely. The increase in the observed  $J(\text{H-Hg})_{vic}$  was probably due to an inductive effect. It may be noted that one of the  $J(\text{H-Hg})_{vic}$ , in (III), involving a proton on carbon not bearing oxygen, is somewhat larger than that involving the proton on the methoxylated carbon. Also,  $J(\text{H-Hg})_{vic}$  in ethylmercuric chloride is larger than those in the oxygenated compounds.

The present conclusions are in substantial agreement with those recently reported by Kiefer and Waters<sup>11</sup>.

The single new geminal H-Hg coupling constant in Table I is very similar to those previously reported.<sup>5,7</sup>

## EXPERIMENTAL

### Materials\*

The method described by Schroeller, Schrauth and Essers<sup>12</sup> for the corresponding bromide was used to prepare 2-methoxyethylmercuric chloride. It had m.p. 67.5–68°

\* All m.p.'s are corrected.

(reported<sup>13</sup> 68–68.5°) and its NMR spectrum is unambiguous proof of structure.

The method of Wright<sup>14</sup> was used to prepare the mixture of deuterated *trans*-4-2-methoxycyclohexylmercuric chlorides from 1,3,3-trideuterocyclohexene, methanol, and mercuric acetate (followed by treatment with sodium chloride to convert the acetate to the chloride). This preparation yields (II) and (IIa) as an inseparable mixture, which should, however, have the same m.p. as the undeuterated compound. The observed m.p. was 111–113° (reported<sup>14</sup>, for the undeuterated compound, 114–115°). The mixture of (II) and (IIa) was converted to the *cis* isomers, (III) and (IIIa), by method "C" of Romeyn and Wright<sup>15,16</sup>. It had m.p. 110–112° (reported<sup>16</sup> for the undeuterated compound, 111–112°).

The ultimate starting material for the 1,3,3-trideuterocyclohexene was cyclohexanone. The  $\alpha$ -hydrogen atoms were exchanged for deuterium by repeated equilibration of the neat ketone with NaOD in D<sub>2</sub>O, as described for acetophenone<sup>17</sup>. Fifty ml (0.5 moles) of the ketone yielded 35 ml (0.34 moles) of tetradeuteroketone after drying and distillation; b.p. 152–157°. This deuterated ketone was reduced to 2,2,6,6-tetradeuterocyclohexanol with 10 g (0.5 mole) of LiAlH<sub>4</sub> in ether. The alcohol was not isolated from the resulting ethereal solution but was converted to the corresponding acetate by the addition of 25 g (0.25 mole) of isopropenyl acetate, one drop of concentrated H<sub>2</sub>SO<sub>4</sub>, and refluxing for 2 h. After neutralization with NaHCO<sub>3</sub>, 35 g (0.24 mole) of 2,2,6,6-tetradeuterocyclohexyl acetate, b.p. 155–172°, was isolated by distillation. The acetate was dissolved in ether and passed twice through an empty glass tube at 400°. The product, 1,3,3-trideuterocyclohexene, was obtained as a mixture still containing about 25% of ether (by VPC) and boiling, 40–60°. The position of the deuterium in this compound was verified by its NMR spectrum, and it was used in the subsequent synthesis without further purification.

Ethoxyethene (8 g, 0.11 mole) was converted to 2,2-diethoxyethylmercuric chloride, (V), by the method of Nesmeyanov, Lutsenko, and Khomutov<sup>18</sup> in 58% yield\*. It is a non-distillable liquid. Its IR spectrum was consistent with the assigned structure and the NMR spectrum described above is unambiguous proof of structure.

Compound (IV) was a gift of Professor TRAYLOR. Its properties are identical with a compound described by Abercrombie *et al.*<sup>19</sup> as "4- $\downarrow$ -acetoxy-1,4- $\uparrow$ -methylene-2- $\uparrow$ -mercuric chloride" in their experimental section. This name contains a trivial error as well as a misassignment of configuration<sup>20</sup>.

Deuteriochloroform was obtained from Merck and Co., Ltd., Canada, and was used without further purification. It showed no extraneous NMR bands other than a low intensity band due to undeuterated material.

### Spectra

Nuclear Magnetic Resonance spectra were obtained on Varian model A-60, HA-100, or 4300 B spectrometers, the latter having been modified so as to be essentially equivalent to model HR-60 and operating at 56.4433 Mc/sec. All measurements at elevated temperature were made on the latter instrument with a Varian heated probe. The temperature was established from the difference between the chemical shifts of the hydroxyl protons and the methylene protons of an external ethylene glycol sample<sup>20</sup>. The published shifts<sup>21</sup> were reduced by a factor 56.4/60.0.

\* We are grateful to Mr. THOMAS S. STRAUB for the preparation of this compound.



For all spectra other than those of (I), a side band was superimposed by means of a Hewlett-Packard 200AB audio oscillator, its frequency determined with a Hewlett-Packard 524-D counter, and peak positions obtained by linear interpolation. To locate the  $^{199}\text{Hg}$  satellites of (I) more precisely, the audio oscillator was modified by putting a  $10^5$  ohm, 10 turn, "helipot" variable resistance across the points R8 and Cr\*. This allowed the sideband frequency to be adjusted to 0.01 c/sec. A sideband of TMS, of about the same amplitude as the satellite, was then carefully superimposed on the central peak of the satellite triplet, and its frequency counted. This technique gives a reproducibility of  $\sim 0.2$  c/sec, which is consistent with the estimated smallest detectable displacement.

## ACKNOWLEDGEMENTS

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## SUMMARY

Vicinal  $^1\text{H}$ - $^{199}\text{Hg}$  coupling constants,  $J(\text{H-Hg})_{vic}$  have been measured for a number of compounds whose stereochemistry is, to varying degrees, known. The results can be rationalized if it is postulated that  $J(\text{H-Hg})_{vic}$  is  $\sim 600$  c/sec when the H and Hg atoms are *trans* and  $\sim 100$  c/sec when they are *gauche*. The chloromercuri group seems to give rise to very small lateral interactions with vicinal atoms and groups, presumably because of its very long bond to carbon.

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\* This modification was suggested by Dr. D. D. ELLEMAN of Jet Propulsion Laboratories.