Long-Range Spin Coupling in Organomercury Compounds

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Proton resonance spectra have been obtained of many compounds of the type CH_3ORHgX, where R is an organic radical and X is chloride, bromide, iodide or acetate. The proton-^{199}Hg spin couplings are tabulated and discussed in terms of R and X. No hindrance to rotation about the carbon-carbon bonds is observed, contrary to previous reports.

Extensive measurements have been made of proton-proton spin-coupling and theories have been postulated which give good agreement with the experimental results.[1,2] Spin coupling of protons to heavy metal atoms is much larger, frequently does not attenuate regularly with an increasing number of chemical bonds between the coupled nuclei and often changes sign along the hydrocarbon chain[3-6]. The aim of this investigation was to obtain a more extensive body of data to aid in understanding the mechanism of proton-heavy atom spin coupling.

The proton resonance spectra of methoxyethylmercuric acetate and hydroxide have been reported.[7] Although the authors report many extra lines, this may be attributed to the weaker magnetic field and poorer resolution available to them. Many of the lines due to the ^{199}Hg spin-coupled satellites would be situated adjacent to the principal peaks under the conditions of their spectra. Hindered rotation about the carbon-carbon bond in methoxyethylmercuric iodide has been postulated from an examination of its infra-red spectrum.[8] However the proton resonance spectrum of this compound, along with all the others reported in this paper, may be most easily explained if free rotation is assumed.

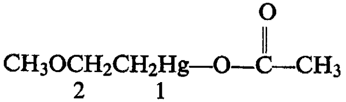
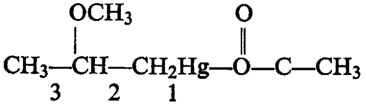
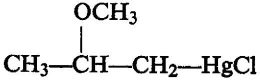
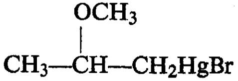
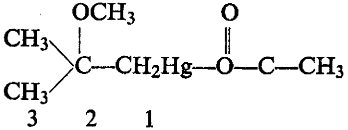
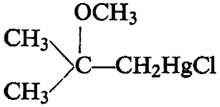
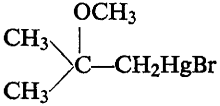
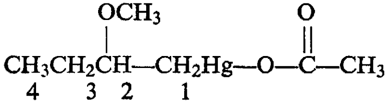
EXPERIMENTAL

The proton resonance spectra were obtained on a Varian Associates high-resolution spectrometer operating at 56·4 Mc, and with the samples at approximately 26°C. Some of the compounds were dissolved in carbon tetrachloride containing 1 % tetramethylsilane. Concentrated or saturated solutions were necessary to obtain a good signal-to-noise ratio for the satellite peaks. Some of the spectra were obtained on the pure liquids in which case the methoxyl group or the terminal methyl group were used as a secondary standard. For these compounds no error is listed beside the appropriate peak in table 1. From cross-checks with other peaks it appears that this procedure does not introduce any error greater than that in determining the peak positions.

Chemical shifts are reported in parts per million to low field of tetramethylsilane, and spin-coupling constants in c/sec. The spectra were calibrated by superposition of audio-frequency side bands generated by a Hewlett Packard model 200J audio oscillator. The modulation frequency was determined to 0·1 c/sec with a frequency counter.

Methoxyethylmercuric iodide was prepared as previously reported.[8] An analysis for mercury yielded 51·3 % compared with the theoretical of 51·9 %. The general procedure followed to prepare the compounds used in this investigation was to bubble the appropriate olefin in excess, into a methanol solution of mercuric acetate. Aliquots of the resultant solutions were evaporated to obtain the acetates. By addition of an equal volume of a methanolic solution of potassium halide to an aliquot of the original reaction mixture, a precipitate of the alkylmercuric halide was obtained. This was filtered if a solid, or separated

TABLE 1.—CHEMICAL SHIFTS OF ORGANOMERCURY COMPOUNDS

compound	δC_{1A}	δC_{1B}	δC_2	δC_3	δC_4	δCH_3O	δX
 $CH_3O\underset{2}{CH_2}\underset{1}{CH_2}Hg{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}CH_3$	2·05 ± ·02		3·59 ± ·02			3·31 ± ·02	1·93 ± ·02
$CH_3OCH_2CH_2HgCl$	2·17 ± ·04		3·63 ± ·04			3·31	
$CH_3OCH_2CH_2HgBr$	2·16 ± ·02		3·68 ± ·02			3·31 ± ·02	
$CH_3OCH_2CH_2HgI$	2·28 ± ·02		3·75 ± ·02			3·30 ± ·02	
 $\underset{3}{CH_3}{-}\underset{2}{\overset{OCH_3}{\overset{\vert}{CH}}}{-}\underset{1}{CH_2}Hg{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}CH_3$	2·02 ± ·02	2·23 ± ·02	3·77 ± ·02	1·23 ± ·02		3·31	1·96 ± ·02
 $CH_3{-}\overset{OCH_3}{\overset{\vert}{CH}}{-}CH_2{-}HgCl$	2·18 ± ·02	2·34 ± ·02	3·94 ± ·02	1·28 ± ·02		3·31	
 $CH_3{-}\overset{OCH_3}{\overset{\vert}{CH}}{-}CH_2HgBr$	2·20 ± ·02	2·37 ± ·02	3·94 ± ·02	1·31 ± ·02		3·31	
	2·21 ± ·02			1·29 ± ·02		3·21 ± ·02	1·96 ± ·02
	2·26 ± ·02			1·29 ± ·02		3·18 ± ·02	
	2·33 ± ·02			1·29		3·19 ± ·02	
 $\underset{4}{CH_3}\underset{3}{CH_2}\underset{2}{\overset{OCH_3}{\overset{\vert}{CH}}}{-}\underset{1}{CH_2}Hg{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}CH_3$	2·12 ± ·02	2·29 ± ·02	4·01 ± ·06	1·54 ± ·06	0·93 ± ·02	3·32 ± ·02	1·97 ± ·02

if a liquid, and dried under vacuum before spectra were obtained. Most of the compounds were unstable to light and heat. This instability increased with increasing atomic weight of halogen and with increasing length of carbon chain. For this reason it was not possible to prepare iodides using olefins larger than ethylene. The spectra of the compounds were obtained shortly after preparation, and following this analyses were performed for mercury. The results of the analyses agreed with the theoretical composition within a few per cent, but were consistently low due to decomposition of the organo-mercury compounds. Best agreement was obtained with the most stable compounds. The proton resonance spectra sometimes showed acetate ion, water or methanol as impurities, generally in quite low concentrations. The corresponding compounds could not be prepared with perfluoro-olefins either by the method just described, or by heating in an autoclave under pressure.

DISCUSSION

The chemical shifts for the protons in the compounds studied are listed in table 1, and the spin couplings in table 2. The spectrum of 2-methoxychloromercuripropane, representative of those obtained, is shown in fig. 1. Except for treatment of the non-equivalent CH_2 protons as an AB system the spectra may be satisfactorily analyzed by first-order perturbation theory. This does not ordinarily allow an assignment of relative signs to the spin-coupling constants. Under certain circumstances it is possible to determine the relative signs even when first-order perturbation is applicable.[9] However, these conditions are not met in the present results. Proton double resonance would be required to determine the relative signs of the mercury-proton spin couplings in these compounds at the magnetic field strength employed.[5] Despite the lack of signs, certain conclusions may still be drawn about the variation in spin coupling with structure.

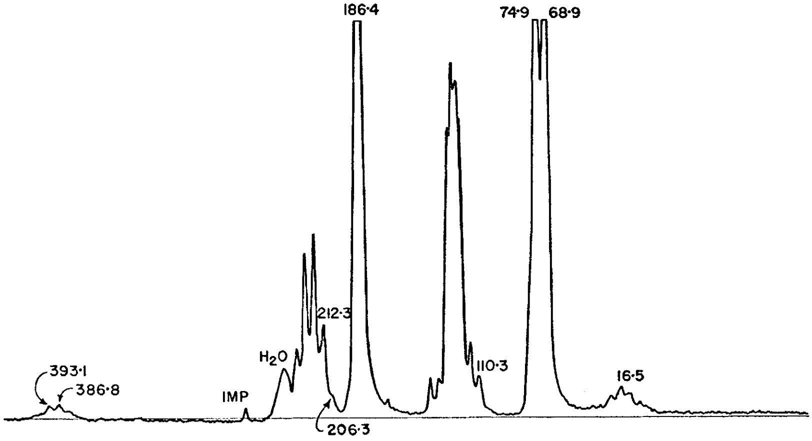
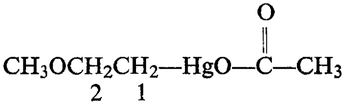
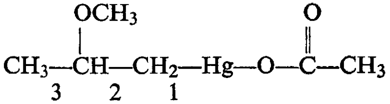
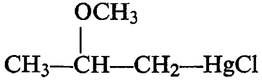
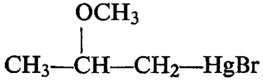
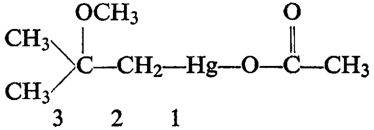
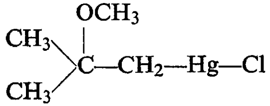
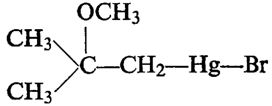
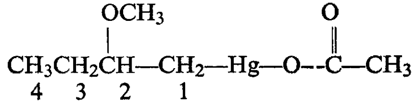


FIG. 1

No satellite peaks due to proton-^{199}Hg spin coupling were observed for methoxyethylmercuric iodide under conditions similar to those for which these peaks were readily obtained with the corresponding chloride, bromide and acetate. It is concluded that rapid exchange is occurring between iodomercuri and methoxyethyl species. Such exchange has previously been observed in organomercury compounds[10] and in other metal alkyls.[5,11] Such exchange was not observed in any of the other compounds investigated.

Spin coupling between ^{199}Hg and the protons on the carbon atom attached directly to mercury are within about 10 c/sec of the value 215 c/sec, regardless of the structure

TABLE 2.—SPIN COUPLING CONSTANTS IN ORGANOMERCURY COMPOUNDS

compound	$JHg—C_{1A}$ $JHg—C_{1B}$	$JHg—C_2$	$JHg—C_3$	$JHg—C_4$	$JC_{1A}—C_{1B}$	$JC_{1A}—C_2$	$JC_{1B}—C_2$	$JC_2—C_3$	$JC_3—C_4$
 $CH_3O\underset{2}{CH_2}\underset{1}{CH_2}—HgO—\overset{O}{\overset{\Vert}{C}}—CH_3$	230 ±2	217 ±2				7·2 ±0·2			
$CH_3OCH_2CH_2—HgCl$	225 ±7	245 ±2				7·0 ±0·2			
$CH_3OCH_2CH_2—HgBr$	207 ±2	249 ±2				6·8 ±0·2			
$CH_3OCH_2CH_2—HgI$	—	—				6·9 ±0·3			
 $\underset{3}{CH_3}—\underset{2}{\overset{OCH_3}{\overset{\vert}{CH}}}—\underset{1}{CH_2}—Hg—O—\overset{O}{\overset{\Vert}{C}}—CH_3$	222 ±4	288 ±8	0		11·9 ±0·2*	5·6 ±0·2*	3·9 ±0·2*	5·7 ±0·5	
 $CH_3—\overset{OCH_3}{\overset{\vert}{CH}}—CH_2—HgCl$	223 ±2	338 ±2	0		13·0 ±0·2	5·8 ±0·2	5·8 ±0·2	6·0 ±0·2	
 $CH_3—\overset{OCH_3}{\overset{\vert}{CH}}—CH_2—HgBr$	205 ±5	295 ±1	0		10·7 ±0·2	5·4 ±0·2	5·1 ±0·2	6·1 ±0·2	
 $\underset{3}{(CH_3)_2}\underset{2}{\overset{OCH_3}{\overset{\vert}{C}}}—\underset{1}{CH_2}—Hg—O—\overset{O}{\overset{\Vert}{C}}—CH_3$	215 ±2		20·8 ±1						
 $(CH_3)_2\overset{OCH_3}{\overset{\vert}{C}}—CH_2—Hg—Cl$	203 ±2		21·1 ±1						
 $(CH_3)_2\overset{OCH_3}{\overset{\vert}{C}}—CH_2—Hg—Br$	204 ±2		21·9 ±1						
 $\underset{4}{CH_3}\underset{3}{CH_2}\underset{2}{\overset{OCH_3}{\overset{\vert}{CH}}}—\underset{1}{CH_2}—Hg—O—\overset{O}{\overset{\Vert}{C}}—CH_3$				0	11·7 ±0·5	4·9 ±0·5	5·4 ±0·5		7·1 ±0·5

* obtained from high field satellite.

of the alkyl chain or the identity of the substituent X. Spin coupling to the protons on the β carbon atom shows a greater variation with X, but no trend is discernible. However, there is a marked increase in the coupling constant for CH compared with CH_2. No spin coupling to the protons on the γ carbon atom is observed in the propyl compounds but a spin coupling constant of 21 c/sec, independent of X, is observed with the sec.-butyl compounds. These results may be rationalized if we assume that the spin coupling is a function of the dihedral angle between the mercury-carbon bond and the bond between the β carbon atom and a proton or methyl group attached to it. A similar relationship has been proposed for long-range proton-proton spin coupling.[12] It has been assumed that the spin coupling is a minimum for a dihedral angle of 180° and gradually increases as the angle approaches 60°.[12]

To explain the present results one must further assume no conformational preference about the α-β carbon bond when only protons and a methoxyl group are attached to the carbon atom. Methyl groups attached to this carbon are assumed to be located as far from the mercury atom as possible. This is shown in fig. 2. The smaller average dihedral angle then corresponds to the larger observed spin couplings. However, if the above conformational preferences are assumed to be true, the larger spin couplings are also associated with a smaller average distance between the coupled nuclei. Direct interaction through space, as has been proposed for some fluorine-fluorine coupling,[13] would also explain the results. Both these hypotheses must be considered quite speculative.

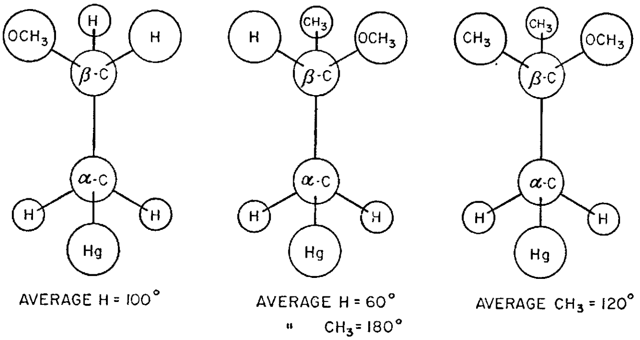


FIG. 2.—Average dihedral angle

The proton-proton spin couplings are similar to those usually observed for alkyl groups. No unusual effects are observed in the proton chemical shifts.

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[1] Karplus, *J. Chem. Physics*, 1959, **30**, 11.

[2] Gutowsky, Karplus and Grant, *J. Chem. Physics*, 1959, **31**, 1278.

[3] Dessy, Flautt, Jaffe and Reynolds, *J. Chem. Physics*, 1959, **30**, 1422.

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[8] Kreevoy and Ditsch, *J. Amer. Chem. Soc.*, 1960, **82**, 6124.

[9] Narasimhan and Rogers, *J. Chem. Physics*, 1959, **31**, 1430.

[10] Reutov, Smolina and Kalyavin, *Doklady Akad. Nauk. S.S.S.R.*, 1961, **139**, 389.

[11] Brownstein, Smith, Ehrlich and Laubengayer, *J. Amer. Chem. Soc.*, 1960, **82**, 1000.

[12] Bothner-By and Naar-Colin, *J. Amer. Chem. Soc.*, 1962, **84**, 743.

[13] Petrakis and Sederholm, *J. Chem. Physics*, 1961, **35**, 1243.