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P.M.R. SPECTRA OF VINYL MERCURIC ACETATE AND BROMIDE

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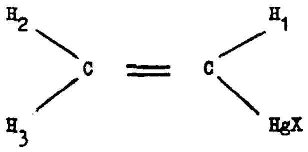
In previous publications,[1,2] the dependences of ^{199}Hg - ^{1}H spin-spin coupling constants on molecular geometry and substituent electronegativities have been demonstrated. Prior to these studies, the only unsaturated mercurials examined were divinyl mercury[3] and the isomeric bis-propenyl mercury compounds.[4] The P.M.R. spectra of unsubstituted vinyl mercurials of the type RHgX have not been previously discussed.

The spectra of vinyl mercuric bromide and acetate were examined in $CDCl_3$, dioxan and acetone solutions. (The spectrum of vinyl mercuric bromide in dioxan is reproduced in Fig. 1.) The spectra were analysed as ABX patterns in three ways, and these results were averaged leading to the set of parameters assembled in Table 1. A satisfactory matching of observed and calculated spectra is obtained with all three proton-proton coupling constants having the same sign.



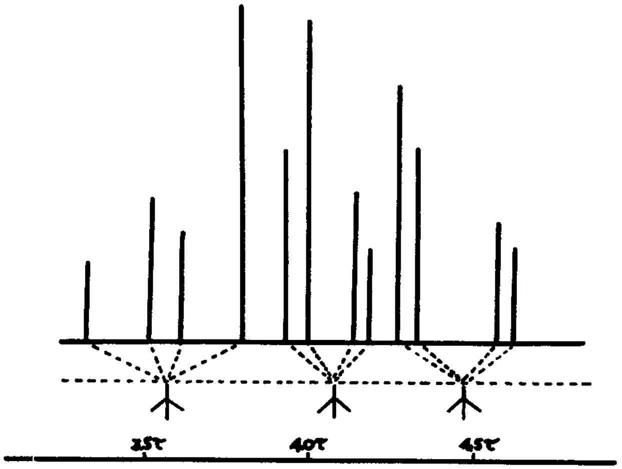


FIG. I

TABLE I

	CDCl$_3$*		DIOXAN†		ACETONE‡	
	X = Br	-OCOCH$_3$**	X = Br	-OCOCH$_3$	X = Br	-OCOCH$_3$
δ_1 (τ)	3.58	3.61	3.55	3.58	3.90	4.04
δ_2 (τ)	4.03	4.08	4.08	4.10	4.47	4.60
δ_3 (τ)	4.52	4.55	4.48	4.50	4.81	4.93
J_{12} (c/s) (cis)	11.7	-	11.9	12.0	11.6	11.5
J_{13} (c/s) (trans)	18.6	-	18.7	18.0	18.8	19.0
J_{23} (c/s) (gem)	2.3	-	3.1	3.0	2.7	3.0
ΣJ	32.6	-	33.7	33.0	33.1	33.5

* Based on internal TMS

** Very dilute solution

† Based on Dioxan 6.38 τ

‡ Based on Acetone 8.33 τ

No pattern corresponding to ^{199}Hg - ^{1}H coupling was observed in any of the bromide spectra, although clearly visible for the acetate in dioxane solution. In this case the following ^{199}Hg - ^{1}H coupling constants were observed:-

$$\left.\begin{array}{ll} \text{(gem)} & \left| J\ ^{199}Hg - {}^{1}H_1 \right| = 291 \text{ c/s} \\ \text{(trans)} & \left| J\ ^{199}Hg - {}^{1}H_2 \right| = 658 \text{ c/s} \\ \text{(cis)} & \left| J\ ^{199}Hg - {}^{1}H_3 \right| = 331 \text{ c/s} \end{array}\right\} \pm 2 \text{ c/s}$$

The shift values and proton-proton coupling constants may be compared with those obtained for other vinyl metallics. (Table 2.)

TABLE 2 (R = Vinyl)

	R Mg Br[5]	R Mg Cl[6]	R Si Cl$_3$[7]	R Li[6]	R_6Ge_2[8]
SOLVENT	T.H.F.	T.H.F.	CDCl$_3$	Et$_2$O	NEAT LIQUID
δ_1 (τ)	3.52	3.32	3.75	-	3.81
δ_2 (τ)	4.02	3.80		-	4.04
δ_3 (τ)	4.34	4.43		-	4.41
J_{12} (c/s)	17.2	17.6	-	19.3	13.3
J_{13} (c/s)	22.1	23.0	-	23.9	20.1
J_{23} (c/s)	7.4	7.5	-	7.1	2.9
ΣJ	46.7	48.1	-	50.3	36.3

The resonance positions for vinyl mercuric bromide and acetate are very similar in CDCl$_3$ and dioxan but suffer a uniform high field shift of ca. 0.35 p.p.m. in acetone (cf Ref. 2), otherwise the proton chemical shifts are very similar to those for other vinyl metallics in a variety of solvents. However, the significance of this similarity cannot be discussed until the structures of organomagnesium and lithium compounds have been fully elucidated. The agreement may be surprising since vinyl lithium and magnesium compounds must possess considerable carbanionic character. In comparison with ethylene (4.70τ, calculated from data[9] at 40 Mc/sec.), all the resonances in the vinyl mercuric compounds are shifted to lower field, the shift being greatest for H_1 (1.12 p.p.m. in the bromide) and least for H_3 (0.18 p.p.m.). Similar observations hold for vinyl magnesium and lithium compounds. A shielding effect, due to the electropositive metal atom might have been anticipated to lead to a high field shift relative to ethylene as observed for metal alkyls.[10] Clearly different factors are dominant in the vinyl series.

Correlations between proton-proton coupling constants and substituent electronegativities have been established for a large number of vinyl compounds.[11] The sum, ΣJ exhibits a good linear dependence on substitutent electronegativity, E_x (Pauling Value). Of added importance is the observation that each of the three coupling constants are linear functions of E_x with nearly the same slope.

The data in the present case is summarized below.

X =	ΣJ	Ex*	Ex
- Hg Br	33.0	~ 2.3	1.9
- Hg $OCOCH_3$	33.0	~ 2.3	1.9
- Mg Br	46.7	~ 1.25	1.2
- Li	50.3	~ 1.0	1.0
- Ge-	36.3	~ 2.10	1.8

* Interpolated from the data of Schaeffer.[11]

This criterion clearly does not distinguish the relative electronegativities of the acetoxy and bromo-mercuric substituents. The interpolated values of Ex are in satisfactory agreement with accepted electronegativities.

The variation of the separate coupling constants, J_{13} (trans), J_{23} (gem), J_{12} (cis), for the above vinyl metallics (Table 1 and 2) is marked. In particular, J_{12} and J_{23} exhibit the largest variations. Extensive calculations[12] have indicated J_{gem} to be a function of the

HCH angle alone, and on this basis, the vinyl mercuric and vinyl germanism compounds (with J ~ 2 to 3 c/s) have a larger HCH angle than vinyl lithium or magnesium compounds (J ~ 7 c/s). The fact that J_{cis}, J_{trans}, J_{gem}, all vary in the same way with the electronegativity of the β - substituent would indicate, that if J_{gem} is a function of the HCH angle, then this angle is a function of the Ex value of the β - substituent.

The absence of a pattern due to $^{199}Hg - {}^{1}H$ coupling in vinyl mercuric bromide indicates vinyl group exchange to be more facile than methyl group exchange and establishes the sequence

vinyl > methyl ~ ethyl; I > Br.

As in the case of methyl mercuric iodide,[13] a four centre concerted pathway seems the most reasonable postulate. This exchange rate is paralleled by the rate of cleavage of dialkyl mercurials with hydrogen chloride,[14] where a similar four centre pathway has been established. We are at present examining a molecular orbital approximation in the hope of providing a rationale of this order.

The magnitude of the coupling constant between ^{199}Hg and its <u>trans</u> proton ($J_{^{199}Hg - {}^{1}H_2}$ = 658 c/s) is the largest yet reported in a mercury system. Large coupling with the trans proton is also observed in <u>cis</u> - 2 chlorovinyl mercuric chloride ($J_{^{199}Hg - {}^{1}H}$ = 474 c/s)[2] and divinyl mercury ($J_{^{199}Hg - {}^{1}H}$ = 296 c/s).[3]

The reduction in coupling constant ($J_{^{199}Hg - {}^{1}H}$) on proceeding from compounds RHgX to R_2Hg is well established[2], although the thoroughly consistent fashion in which it is reduced has not been previously demonstrated. Since in compounds of the type RHgX, the nature of X appreciably alters $J_{^{199}Hg - {}^{1}H}$,[1] the demonstration will be restricted to compounds in which X = Cl or $-OCOCH_3$. Clearly, any series of mercurials having the same -X substituent in RHgX could have been selected, though the reduction ratio would be correspondingly altered.

A plot of the coupling constants in RHgX against the coupling constants in the corresponding R_2Hg compounds shows a fairly accurate linear relationship

$$J\ (RHgX) = 2.2\ J\ (R_2Hg)$$

for R = gem, cis and trans in vinyl, gem and cis in trans 2 - chlorovinyl, methyl, α and β in ethyl and $-CH_2\ CO_2^-$.

Apart from any theoretical implications this relationship permits the prediction of ^{199}Hg - ^{1}H coupling constants and has proved valuable in structure elucidation.[13]

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