Tetrahedron Letters No. 23, pp. 1531-1534, 1963. Pergamon Press Ltd.
Printed in Great Britain.

P.M.R. SPECTRUM OF 2-HYDROXYETHYL MERCURY(II) HYDROXIDE.

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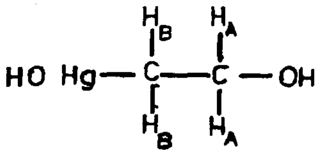
(Received 16 July 1963)

The proton magnetic resonance spectra of mercury(II) addition compounds of ethylene have been examined by Cotton and Leto(1) to provide evidence for the formulation as σ-bonded compounds. The simplest compound 2-hydroxyethyl-mercury(II) hydroxide, examined in KOH/D_2O solution at 40 Mc/s, provided such evidence but "the appearance of shoulders on the central components of the triplets" was considered puzzling and was unexplained.

The carbon bound protons of



2-hydroxyethylmercury(II)hydroxide constitute a four spin system classified as A_2B_2 if there is rapid rotation about the C-C bond or if rotation is restricted with the molecule in the trans conformation. (The symmetrical appearance of the spectrum excludes a gauche conformation). Under these circumstances with two different H_A-H_B spin-spin coupling constants (transoid J_T and cisoid J_C) the more complex pattern observed by Cotton and Leto is the expected one.

We have re-examined the spectrum at 60 Mc/s, obtaining greater peak separations, and successfully analysed the spectrum as a simplified A_2X_2 system. The simplification arises from the facts that the two coupling constants J_{AA} and J_{BB} are essentially equal and that their sum is considerably greater than the difference $|J_T-J_C|$. A pattern of two quintets centred on the resonance positions of H_A and H_B each with intensities in the ratio 2:1:2:1:2 is expected. The observed pattern differs slightly since H_A and H_B are not sufficiently different to completely satisfy the A_2X_2 condition.

By comparison with the p.m.r. spectrum of 1-propanol(2) the observed resonance positions may be assigned as below.

CH_3-CH_2-CH_2-OH in $CDCl_3$

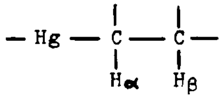
8.43τ 6.42τ

HO Hg - CH_2 - CH_2 - OH in D_2O

8.27τ 6.34τ

These are in good agreement with the findings of Cotton and Leto. It may also be deduced from the spectra that J_T = 9.8 and J_C = 6.4 c/s in agreement with the values J_T = 9 and J_C = 6 c/s found by Pople, Schneider and Bernstein(3) for 1,2-chlorobromoethane.

The observation in our spectrum of low intensity patterns on the high field and low field sides of the two quintets due to ^{199}Hg - ^{1}H couplings provides final proof of the presence of a Hg-C σ-bond(4). The magnitudes of the observed coupling constants are $J_{^{199}Hg-H\alpha}$ = 217.5 c/s and



$J_{^{199}Hg-H_\beta}$ = 159 c/s. For a series of compounds of the type CH_3HgX the methyl resonance positions and ^{199}Hg - ^{1}H coupling constants are recorded in Table 1.

TABLE 1.

X in CH_3HgX	D_2O solution τ-value	D_2O solution $J_{^{199}Hg-^{1}H}$	Dioxane solution τ value	Dioxane solution $J_{^{199}Hg-^{1}H}$
ClO_4	8.79	260		
$OCOCH_3$	9.05	232	9.08	220
Cl			9.07	211
Br			8.98	207
I			8.91	- *
CN	9.40	188	8.88	175

* No coupling is observed since a rapid methyl group exchange between ^{199}Hg and ^{200}Hg is presumably taking place (cf. 5).

It can be seen that the effect of the mercury atom on the resonance position of a methylene group is small and towards high field justifying our assignments. (The methylene groups of paraffins absorb at ca. 8.8τ in $CDCl_3$ solution(2).

A marked dependence of $J_{^{199}Hg-^{1}H}$ on the nature of X in CH_3HgX is evident from the data of Table 1. From a more detailed study by Schneider(6) it appears that the present value of $J_{^{199}Hg-^{1}H}$ is characteristic of the system HO-Hg-CH.

The value of $J_{^{199}Hg-H_\beta}$ is however distinctly different from those previously observed. Schneider(6) finds that in CH_3CH_2HgX, $J_{^{199}Hg-H_\beta}$ is consistently 30-40% larger than $J_{^{199}Hg-H_\alpha}$. Similar observations have been made for mercury dialkyls(7). Baker(8) reports that in $(C_2H_5)_4Pb$, $J_{207Pb-H\beta}$ exceeds $J_{207Pb-H\alpha}$, and Burke and Lauterbur(9) report similar finding for $^{119}Sn-^{1}H$ couplings. It is noteworthy that in all these compounds there are no substituents on C_β while in the present example this carbon bears a hydroxy-group. We are at present investigating compounds of the type XHg.CHR-CHRR to determine the extent to which α and β-substituents modify the ^{199}Hg - ^{1}H coupling constants. Present results indicate that the methyl-group in $CH_3.CH_2HgX$ leads to a very small increase in $J_{199Hg-H\alpha}$, while the $-CO_2^-$ group in $HO-Hg-CH_2CO_2^-$ (10) ($J_{199Hg-1H}$ = 265 c/s) leads to a considerable increase.

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