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^{13}C - ^{199}Hg SPIN COUPLING IN ALKYLMERCURIALS: A USEFUL ANGULAR DEPENDENCE OF VICINAL COUPLING

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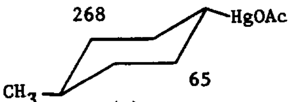
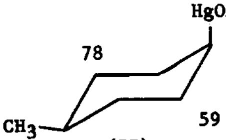
Recently we reported[2] the great utility of ^{13}C nmr spectroscopy in the study of conformational equilibria in cyclohexylmercury systems and inter alia the observation of a pronounced dihedral angle dependence of vicinal ^{199}Hg - ^{13}C coupling. We now wish to report the salient features of more general studies of ^{13}C - ^{199}Hg coupling[3] in anticipation that such data will facilitate structural and conformational conclusions in this important area.

Compounds of essentially fixed molecular geometry were examined and spectral assignments were made by consideration of off-resonance decoupled spectra, chemical shifts and signal intensities. In addition, it was clear that four-bond coupling was small ($\ngtr$ 10 Hz) and that one-bond coupling was comparatively large (1500-1700 Hz). As ^{199}Hg has a 17% natural abundance the ^{13}C coupling to this isotope is observed in the form of satellites in the main ^{13}C spectrum.

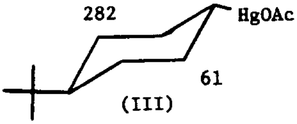
The trans (I) and cis (II) 4-methylcyclohexylmercuric acetates (of established configurations)[4] indicated that vicinal ^{199}Hg - ^{13}C coupling was strongly dihedral angle dependent as the coupling constants (Hz) below demonstrate for $\theta = 180°$ (I) and $\theta = 60°$ (II).



(I)



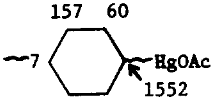
(II)



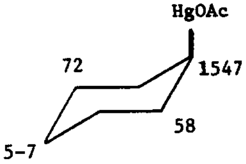
(III)

Similar values to those for (I) are found for trans-4-t-butylcyclohexylmercuric acetate (III).

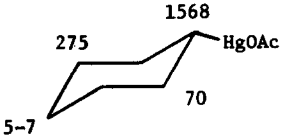
Cyclohexylmercuric acetate itself at ambient probe temperature (where conformational interconversion is rapid) exhibits averaged coupling constants as shown on structure IV. At lower temperatures signals for the axial (V) and equatorial (VI) conformers (ca. 2:1)[2] are observed and the coupling constants indicated, have been measured. Using (I) and (II) as models for equatorial - HgOAc and axial HgOAc, respectively, it is clear the assignments in (V) and (VI) are the only acceptable ones, and that 4-alkyl substitution has a rather minor effect on these couplings.



(IV)

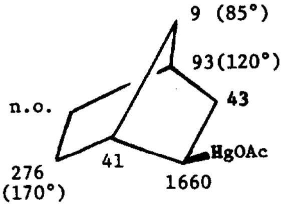


(V)

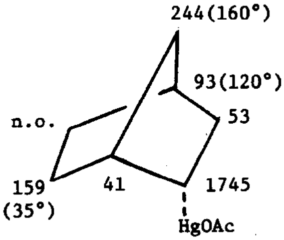


(VI)

Exo (VII) and endo (VIII) 2-norbornylmercuric acetates are particularly instructive with respect to $\underline{\text{vic}}J_{\text{Hg-C}}$, since three ($\theta$,J) combinations are provided by each compound.



(VII)



(VIII)

Quantities in parentheses are estimated dihedral angles for the given $\underline{\text{vic}}J_{\text{Hg-C}}$

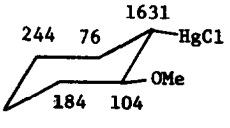
n.o. = not observed

Compounds I-VIII then furnish the following (θ,*J*) combinations, for solutions in $CDCl_3$:

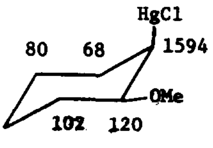
θ :	35°	60°	85°	120°	160°	170°	180°
J :	159	78,72	9	93	244	276	268, 275, 282

The (*J*,θ) plot is clearly a curve of the Karplus form, and the rather large variation in *J* with θ should allow useful deductions regarding the geometry of alkylmercury systems. This type of angular dependence of $^{vic}J_{M-C}$ where M = Sn[5], Hg, Pb[6] and (apparently) Tl[7], may well be a general phenomenon for sp^x M-C systems, and hence constitute a key structural criterion, since these couplings are readily observed, with the *J* values being comparatively large. From the point of view of spectral assignment, the large one-bond coupling (1500-1800 Hz) is noteworthy, as is the relative constancy of two-bond coupling (40-70 Hz). One-bond coupling in the *endo*-2-norbornyl derivatives of Sn[5] and Hg is significantly larger (≃ 5%) than in the *exo* compounds (432, 416 Hz for Sn, 1745, 1660 Hz for Hg) and again reflects the differing steric and/or electronic environments in these situations. (One-bond couplings in **axial** and **equatorial** cyclohexylmercuric acetates are 1547 and 1568 Hz respectively).

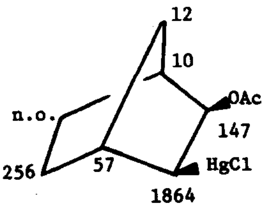
A number of oxymercurials, of which IX - XII are exemplary, have also been examined. The results indicate that cmr spectroscopy will be extremely valuable in structure determination for this important class of mercurial, particularly since the stereochemistry of oxymercuration is variable.[8] Note that the electronegative oxyfunctions appreciably increase coupling to the oxygenated carbon, presumably by affecting the "effective nuclear charge" term. Perturbations in opposite directions of $^{vic}J_{Hg-C}$ by the attachment of an oxygen function to C(2) in the sequence $^{13}C(3)-C(2)-C(1)-Hg$ are seen in IX and X (cf. I and II, or V and VI) and would result from different torsional angles in IX and X associated with the vicinal coupling. Examination of a larger range of oxymercurials is underway to understand more fully structural and intramolecular coordination effects on these couplings.



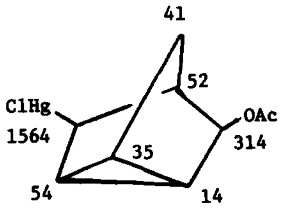
(IX)



(X)



(XI)



(XII)[9]

A discussion of chemical shifts will be given in a subsequent full report of our cmr studies of organomercurials, but we wish to draw attention to the following "substituent effects" of the -HgOAc group in cyclohexyl compounds: α,β,γ and ε effects of ca. + 20, + 5, ≃ 0 and -2.0 ppm respectively. These effects should also be useful in considering assignments of cmr spectra.

Compounds I - XII are known, and had m.p.'s and ^1H spectra in agreement with the literature and/or the indicated structures.

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References

1. Queen Elizabeth II Fellow at University of New England Armdale NSW 1972-1974.
2. F. A. L. Anet, J. Krane, W. Kitching, D. Doddrell and D. Praeger, Tetrahedron Lett., 3255 (1974).
3. For some previous measurements see F. T. Weigert and J. D. Roberts, Inorg. Chem., **12**, 313 (1973).
4. F. R. Jensen and L. H. Gale, J. Amer. Chem. Soc., **82**, 145 (1960). These configurations are confirmed by 100 MHz ^1H nmr spectra.
5. A similar demonstration has been reported for alkyltin and some other systems: D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila and R. H. Sarma, ibid, **96**, 1640 (1974) and references therein.
6. Unpublished results.
7. Research in progress.
8. W. Kitching, Organometal. Reactions, **3**, 330 (1972) and references therein.
9. The couplings to the cyclopropyl carbons, while consistent with chemical shifts and "Hg - substituent effects", should be regarded as tentative.