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CONFORMATIONAL ANALYSIS OF β-METHOXY-β-PHENYLETHYLTHALLIUM(III) COMPOUNDS: EVIDENCE FOR TRANS ADDITION IN OXYTHALLATION OF STYRENE

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^{1}H NMR conformational analysis of the title compounds derived from styrene and β-styrene-d provided evidence for trans addition in oxythallation of styrene.

Recently Uemura et al. observed a large difference in the values of $^2J_{TlH}$ for two non-equivalent α-proton resonances in the ^{1}H NMR spectra of $PhCH(OR)CH_2Tl(OCOR')_2$ 1 without any reasonable interpretation for such a rather unusual observation.[1] We wish to present a most likely explanation for this phenomenon in terms of a restricted rotation about the C_α-C_β bond and β-substituent effects on $^2J_{TlH}$, and describe one significant implication of the results of such an analysis, i.e. clear evidence of trans addition in oxythallation of acyclic olefins.[2]

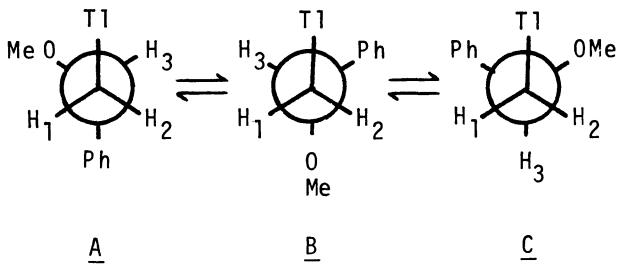
The Table shows chemical shifts and J_{TlH} of relevant proton resonances for 1a (R= R'= Me) and $PhCH(OMe)CH_2Tl(dtc)_2$ 2.[3] We have assigned these resonances as due to the protons shown in the figure below for the following reasons. Of the two diastereotopic α-proton resonances, one pair with the smaller $^2J_{TlH}$ appears as broad triplets ($^2J_{HH} \simeq {}^3J_{HH} \simeq 10.5$ Hz) and the other pair with the larger $^2J_{TlH}$ as broad doublet of doublets ($^2J_{HH} \simeq 10.5$, $^3J_{HH} \simeq 5.0$ Hz), suggesting that either A or B exists as the dominant conformer even at 25°.[4] We propose that A is more stable than B in view of the relative size of the phenyl and methoxy groups. Probably then, the order of the degree of

^{1}H NMR Data[a] for 1a and 2 in $CDCl_3$.

	δ [J_{TlH}]					
	1a			2		
Temp.	H_1	H_2	H_3	H_1	H_2	H_3
25°	3.07 [753]	3.16 [903]	4.62 [738]	2.76 [534]	2.79 [670]	4.66 [572]
-50°	2.96 [706]	b) [ca885]	b) [ca610]	2.77 [487]	2.73 [665]	4.52 [460]

a) At 60 and 100 MHz. δ in ppm, J in Hz.

b) Too broad to determine precisely.



A B C

contribution to the observed spectra is A ≫ B ≫ C. From this predominance of A, it is indicated that $^2J_{TlH_1}$ is smaller than $^2J_{TlH_2}$, and this is understandable if the theory[5] of β-substituent effects on $^2J_{HH}$ can be allowed to apply in the case of $^2J_{TlH}$.[6] Thus, the methoxy group, a strongly electron-withdrawing substituent, gauche to Tl and H_1 as in A would cause a small positive shift of $^2J_{TlH_1}$ relative to that in unsubstituted β-phenylethylthallium(III) compounds, while negative shifts are expected for $^2J_{TlH_2}$ in A and for $^2J_{TlH_1}$ and $^2J_{TlH_2}$ in B, all in approximately similar magnitudes. At -50°, the contribution of A to the spectra would become more important at the expense of those of B and, to a lesser extent, C,[4] resulting in a decrease of $^2J_{TlH_1}$, but very little change in $^2J_{TlH_2}$ as indeed found. Also, only a slight decrease in the concentration of C would be enough to explain a decrease in $^3J_{TlH_3}$ at the lower temperature, since $^3J_{TlH_3}$ is expected to be much more configuration dependent in view of the reported ratio, $^3J_{HgH(trans)}/^3J_{HgH(gauche)} \geq 6$, in organomercury(II) compounds.[7]

The spectrum of 1a-d prepared by the reported method[1] using trans-PhCH=CHD exhibited no resonances due to H_1, and integration of the peaks due to H_2 and H_3 indicated 100 % trans addition of the $Tl(OAc)_2$ and methoxy groups to styrene under the conditions employed. The occurrence of the restricted rotation in 1a and 2, but not in analogous oxymercurated adducts of styrene,[8] may probably reflect a greater steric interaction between the β-substituents and the thallium-bound ligands,[9] and an analysis of other oxythallated products of olefins similar to that described above will prove useful in stereochemical studies of oxythallation.

References and Notes

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2) For stereochemistry of oxythallation of cyclic olefins, see W. Kitching, Organometal. Chem. Rev. A, 3, 61 (1968); A. McKillop, M. E. Ford, and E. C. Taylor, J. Org. Chem., 39, 2434 (1974).

3) dtc= $SSCNMe_2$. 2 was prepared from 1a and Na(dtc) in methanol.

4) It was difficult to see any temperature dependence of J_{HH} definitively because of the broadness of the resonances, particularly at the lower temperatures.

5) J. A. Pople and A. A. Bothner-By, J. Chem. Phys., 42, 1339 (1965).

6) It was shown that $^2J_{TlH}$, like $^2J_{HH}$, are negative in sign and dominated by the Fermi contact term; J. P. Maher and D. F. Evans, J. Chem. Soc., 637 (1965).

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