

Preliminary communication

Magnetic non-equivalence of methyl groups in organotin compounds

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(Received May 17th, 1972)

Recent communications have described the magnetic non-equivalence of methyl and methinyl protons adjacent to a chiral tin atom¹ and the non-equivalence of methyl groups on tin bound to a chiral carbon atom². These reports prompt us to present our own results in this field. We have prepared the dimethyltin diamines (Ia) and (Ib) by stirring 1-(dimethylamino)methyl-2-lithioferrocene with dimethyltin dichloride in diethyl ether. The 2-substituted metallocene group contains a chiral plane³ and the diamine (I) was isolated in the *meso* (Ia) and racemic (Ib) forms⁴. The isomers were distinguished by treatment of the methiodides of each with (+) α -methylbenzylamine when the cyclic amines (IIa and b; R = NCHMePh) respectively were obtained. The compound (IIa; R = NCHMePh) was characterised in one form only while (IIb; R = NCHMePh) was obtained as two diastereoisomers with different optical rotations.

The chemical shift difference between the methyl groups bound to tin in the compound (Ia) was markedly solvent dependent (see Table 1), with a four-fold change in $\Delta\nu$ between benzene and chloroform. The effect of solvent on the cyclic amine (IIa; X = NPh) was less marked, only a 7% change between the same two solvents was observed although the $\Delta\nu$ values were much larger. These results concur with the greater conformational rigidity in compound (IIa) than in (Ia) and emphasize the importance of conformational effects in this system. Changes in the size and electronegativity of the bridging group (X) in the compound (IIa) gave only small changes in $\Delta\nu$. The diamine (Ia) in chloroform showed an initial decrease in $\Delta\nu$ with increasing temperature and a constant value was observed at higher temperatures. In toluene, the chemical shift difference increased with increasing temperatures before assuming a constant value at higher temperatures. A similar dependence was observed for the C-methyl groups of 1-isopropyl-2-(dimethylamino)methylferrocene in aromatic solvents⁵ and for ethyl- and t-butyl dimethyl(α -methylbenzyl)tin². The effect cannot be attributed wholly to the characteristic ability of benzenoid aromatics to solvate electron deficient sites in the solute molecule and causes specific effects⁶ since the cyclic compound (IIa; X = NPh) in chloroform showed a similar increase in $\Delta\nu$ with a rise in temperature. Also, normal temperature dependence of *gem*-dimethylsilane derivatives in toluene has been reported recently⁷. The limiting value of $\Delta\nu$ at higher temperatures has been interpreted as a measure of intrinsic dissymmetry⁷, such an interpretation cannot be applied directly to

