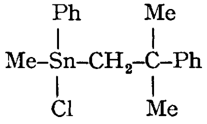
Molecular Asymmetry and Magnetic Nonequivalence in Organometallic Compounds. Rapid Inversion of an Asymmetric Organotin Chloride

By G. J. D. PEDDLE
(*Department of Chemistry, University of Alberta, Edmonton, Canada*)
and G. REDL
(*Department of Chemistry, New York University, University Heights, New York* 10453)

IN recent mechanistic studies optically active organosilicon[1] and organogermanium[2] compounds were used. Attempts to extend these studies to include the stereochemistry of reactions of organotin compounds or to repeat the resolution of n-propylethylmethyltin iodide reported by Pope and Peachey[3] have been unsuccessful.[4] We report the results of a study of the n.m.r. spectrum of ββ-dimethylphenethylmethylphenyltin chloride (I) which indicates that the failure to isolate optically active organotin halides may be due to the rapid inversion of the organotin compound.†



$$\mathrm{Me{-}\overset{\displaystyle Ph}{\underset{\displaystyle Cl}{Sn}}{-}CH_2{-}\overset{\displaystyle Me}{\underset{\displaystyle Me}{C}}{-}Ph}$$

(I)

In the n.m.r. spectrum of dilute solutions of (I) (0·7M) at 38° in benzene, carbon tetrachloride, and toluene, the signals corresponding to the diastereotopic methyl protons of the ββ-dimethylphenethyl group appeared as clearly separated peaks (τ 8·53 and 8·63 in CCl_4). When the concentration of (I) was increased the temperature at which coalescence of the doublet into a singlet occurred decreased from *ca.* 70° for a 1·1M-solution of (I) in benzene to *ca.* 20° for a 3·3M-solution.

In a more polar solvent such as CH_2Cl_2 the temperature at which coalescence occurred was markedly decreased. Thus the diastereotopic methyl peaks in the n.m.r. spectrum of a 0·9M-solution of (I) in methylene chloride coalesced at −40°.

Coalescence of the methyl peaks was also brought about by the addition of comparatively small amounts of good ligands such as acetone or dimethyl sulphoxide. The addition of 2 μl. of dimethyl sulphoxide to 400 μl. of a 0·7M-solution of (I) in benzene caused the signals to merge into a singlet. When the solution was evaporated and the residue redissolved in benzene, the original spectrum with separated methyl peaks was obtained.

The dissimilar environments for the methyl groups of (I) could arise either from restricted rotation of the ββ-dimethylphenethyl or from diastereotopic shielding by the neighbouring asymmetric tin centre. In diphenyl-ββ-dimethylphenethyltin iodide and bromide, which lack the asymmetric tin centre, the two methyl groups gave a sharp singlet indicating that the separation in (I) is not due to restricted rotation. In addition, the concentration dependence of the spectrum of (I) would be difficult to rationalize in terms of restricted rotation.

The observed results are therefore best explained in terms of diastereotopic shielding of the methyl

† The mean lifetime of the inverting species at coalescence is estimated to be of the order of 0·045 seconds.

groups by the asymmetric tin atom. Rapid inversion of the asymmetric tin centre would lead to effective averaging of the environment of the two methyl groups on the n.m.r. time scale and result in coalescence of the two peaks.

The low ionizing-power of the media speaks against an inversion involving primarily chloride-ion displacement. At least in the case of the added dimethyl sulphoxide an expanded octet mechanism similar to that proposed for the racemization of 1-naphthylphenylmethylfluorosilane[5] seems more likely. In the absence of added ligands, halide exchange (possibly involving a symmetrical intermediate or dimer) such as recently observed[6] may be involved. As the concentration of a benzene solution of (I) was increased from 0·01M to 0·2M, the apparent molecular weight of (I) increased from 370 to 405.

The addition of trimethyltin chloride to a benzene solution of (I) also caused merging of the diastereotopic methyl peaks, again indicating that association of organotin chloride molecules is sufficient to cause racemization.

We thank the Petroleum Research Fund and the National Science Foundation for financial support.

(*Received, April 2nd*, 1968; *Com.* 414.)

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