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Preliminary communication

An apparent *syn* Beckmann rearrangement of a stannyl ketoxime

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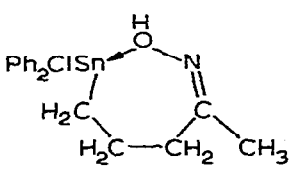
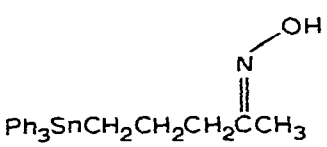
SUMMARY

Chloro(4-oximinopentyl)diphenyltin was shown to have the cyclic structure A: when this compound was treated with phosphorus pentachloride the product arising from exchange of groups which are *syn* to each other was obtained.

All previous experience with organotin monochlorides, R_3SnCl, indicates that, for chloro(4-oximinopentyl)diphenyltin (I), a 5-coordinate structure will be preferred[1]. This raises questions as to whether coordination of the oximino group to tin will be via oxygen or nitrogen and whether the coordination will be intramolecular or intermolecular. All the physical measurements (the salient features of which are given below) made on I indicate that it has structure A. 4-Oximinopentyltriphenyltin (II), on the other hand, is expected[1] to have a structure (such as B) containing 4-coordinate tin and this is confirmed by spectral measurements.



(A)



(B)

For example, II exhibits hydrogen bonding in the solid state as evidenced by the broad ν(O–H)assoc. bands at 3240 and 3150 cm^{-1} in the IR spectrum[2]; these bands decreased in intensity when spectra of II in solution (CCl_4 or $CHCl_3$) were measured and the sharp ν(O–H)free band appeared at 3575 cm^{-1}. By contrast, I does not exhibit hydrogen

bonding and shows only a sharp ν(O–H)free band at 3475 cm^{-1} irrespective of physical state or the concentration in solution. The lower frequency of the ν(O–H)free band in I compared with II is consistent with the lower electron density at oxygen in I[2]. The ν(C=N) band in I is in the normal[3] position at 1651 cm^{-1}.

The NMR spectrum of I confirms the formulation A and supports the *syn*-methyl configuration for II shown in B. In oximes of methyl ketones the signal from the methyl protons occurs at higher field when CH_3 is *syn* to the OH group than when it is *anti*[4]. In methyl propyl ketoxime (equilibrium mixture of isomers[5] in deuterobenzene) these resonances occur at τ8.34 (*syn*-methyl) and τ8.26 (*anti*-methyl). Compound I shows the methyl proton resonance at τ8.15 ($CDCl_3$) and compound II at τ8.40 ($CDCl_3$).

Compound I underwent a Beckmann rearrangement on treatment with phosphorus pentachloride to give the product, $CH_3CONHCH_2CH_2CH_2SnClPh_2$, resulting from the exchange of *syn* OH and stannylpropyl groups. When II was treated with the same reagent a phenyl group was replaced by a chlorine atom. Compound II was rearranged without cleavage of Sn–C bonds by heating the tosyl ester in aqueous alcohol to give, again, an *N*-substituted acetamide, $CH_3CONHCH_2CH_2CH_2SnPh_3$ which, in this case, arose from the more usual exchange of groups in the *anti* configuration.

Using NMR spectroscopy it is now possible to assign configurations to ketoximes but this information may be of little value because of rapid equilibration of isomers. This is particularly true for aliphatic ketoximes which do not usually show the high degree of stereospecificity in the Beckmann rearrangement which is associated with aromatic ketoximes. The rearrangement of I is unusual in two respects, firstly the starting material is an aliphatic ketoxime fixed in a known configuration and secondly, it appears that *syn* groups are exchanged. The most likely explanation for the latter point is that an intermediate ester is formed containing an N–O–P linkage lowering the electron density at oxygen causing scission of the O→Sn bond in A. Inversion of configuration at nitrogen would occur at this step followed by a normal exchange of groups in the *anti* positions.

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