ORGANOTIN CHEMISTRY

VII[*]. THE NMR SPECTRA OF A DISTANNOXANE[**]

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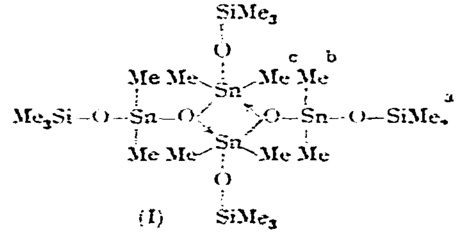
INTRODUCTION

Okawara[2] determined, from an X-ray analysis, that tetramethyl-1,3-bis-(trimethylsiloxy)distannoxane has structure (I). The establishment of this structure on such firm grounds is a significant advance in understanding the chemistry of the partial hydrolysis products of diorganotin derivatives of a wide variety of active hydrogen compounds[3,4]. Since it was reported that (I) was dimeric in solution[2] it presented to us an opportunity to study this interesting structure by proton NMR.

Three different types of protons may be recognized in (I). Those contained in the methyl groups attached to silicon we have designated as (a) protons. The exocyclic tin atoms have a coordination number of four and the protons in their methyl groups, (b) protons, are distinguishable from the (c) protons in the methyl groups attached to the penta-coordinate tin atoms in the ring.



(I)

EXPERIMENTAL DETAILS

The Varian A-60, HR-60, and HR-100 NMR spectrometer systems were each employed for various aspects of the investigation. The A-60 was used for spectra calibration and variable temperature observation at 40° and above.

The HR-60 with variable temperature accessory and integrator supplied the

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60 Mc thermodynamic data. The temperature range was limited on the high side by poor resolution (the two lines are only 5.5 cps apart at 40°) and on the low side by the fact that solute seperated below 15°. The 60 mc RF field was set sufficiently low to eliminate possible errors due to RF saturation of the resonance lines. The sample temperatures are accurate to ± 1°. The HR-60 was also used for the 19.250 Mc ^{119}Sn resonance.

The HR-100 verified the chemical non-equivalence of the hydrogen resonances arising from the methyl groups attached to the tetra- and penta-coordinate tin nuclei and, additionally, provided a well resolved spectrum of the high-field tin satellites which, at 60 Mc, are completely masked by the resonance arising from the methyl groups attached to silicon (see Fig. 1).

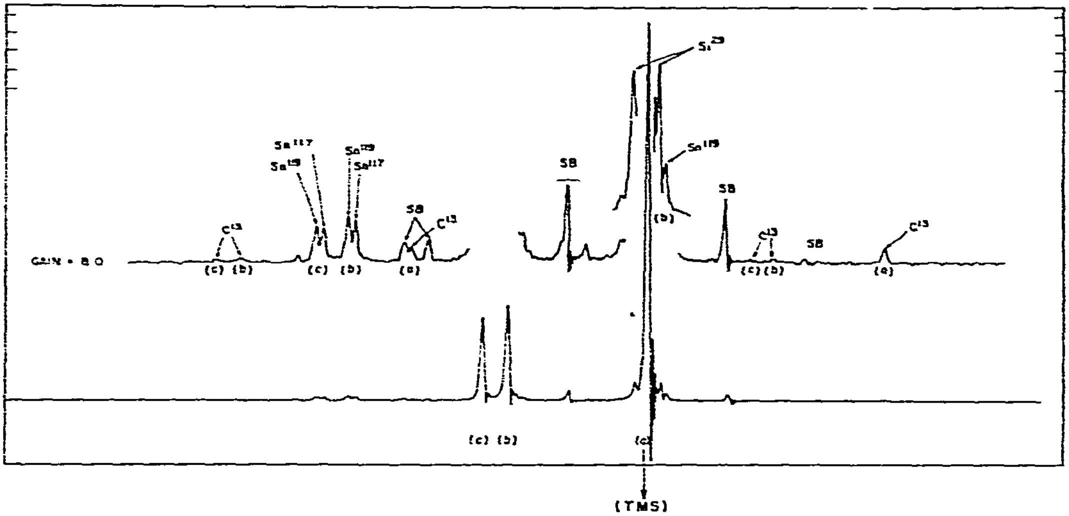


Fig. 1. 60 Mc proton NMR spectrum of (I).

Tetramethyl-1,3-bis(trimethylsiloxy)distannoxane (I) was prepared according to the method of Okawara[5]; m.p. 167–8° (uncorr.) Lit.[5] 167–8°.

RESULTS

With the exception of the chemical shift determination, all proton resonance investigations were obtained with the same carbon tetrachloride solution (*ca.* 15 %) of (I) which has been sealed in a standard Varian analytical sample tube. The chemical shift values listed in Table 1 are relative to internal tetramethylsilane and were obtained at 40°. The readings were taken directly from an A-60 precalibrated chart of 100 cps total sweep range, which assures an accuracy of ± 0.5 cps (± 0.008 ppm). The spin–spin coupling constants listed in Table 2 were obtained as in the case of the chemical shifts; however, a precalibrated chart of 250 cps total sweep range was used and therefore an accuracy of ± 1 cps should be applied.

A saturated solution of (I) in CCl_4 at room temperature provided two, equally intense ^{119}Sn resonances as in the case of $Bu_4Sn_2Cl_2O$ and $Bu_4Sn_2Br_2O$ reported by

Alleston *et al.*[2]. The chemical shift of these two tin resonances were measured relative to that of tetramethyltin and occurs at 130 ± 2 and 156 ± 2 ppm higher-field values than the reference compound. The referencing was accomplished by immersing a 5 mm O.D. sample of $(CH_3)_4Sn$ within the 15 mm O.D. sample of (I) and using a dispersion mode, 2 kc-field modulation, first sideband presentation. Calibration of the chart was accomplished by accurately measuring the 2 kc with a frequency counter.

TABLE 1

CHEMICAL SHIFTS

Relative to internal TMS (ppm)

$\delta_a = -0.05$

$\delta_b = 0.54$

$\delta_c = 0.63$

TABLE 2

COUPLING CONSTANTS (± 1.0 cps)

$J(H_a-{}^{13}C)$	116.3
$J(H_b-{}^{13}C)$	130.5
$J(H_c-{}^{13}C)$	133.8
$J(H_a-{}^{29}Si)$	6.3
$J(H_b-{}^{117}Sn)$	74.0
$J(H_b-{}^{119}Sn)$	77.8
$J(H_c-{}^{117}Sn)$	79.0
$J(H_c-{}^{119}Sn)$	82.0

During this investigation, a typographical error was found to exist in the Varian Associates NMR Table (a listing of various nuclear constants pertinent to nuclear resonance). The resonant frequency in a 10 kilogauss magnetic field for the ^{117}Sn nucleus should be 15.17 Mc instead of 15.77 Mc.

The proton spectrum of (I) is reproduced as Fig. 1. Of the three major peaks, that marked (a) can be unequivocally assigned to the silyl methyl groups because its area is approximately 1.5 that of the sum of the areas of (b) and (c), which is the relative abundance of the types of protons present. Further, the characteristic ^{29}Si–H coupling satellites, which can be recognized from their symmetrical disposition around the (a) peaks reinforce this assignment. The two remaining proton peaks are assigned to the (b) and (c) protons on the basis of the following argument.

Fig. 2 shows the effect of increasing temperature on the (b) and (c) peaks of the spectrum. With increasing temperatures the (c) peak disappears and is incorporated into the (b) peak, which survives alone at 85°. The (c) peak which disappears at higher temperatures, is the resonance ofthe methyls attached to the penta-coordinate tin atoms. These assignments arise from a consideration of the structure of (I). The ring is held together by coordinate bonds which would be expected to dissociate at

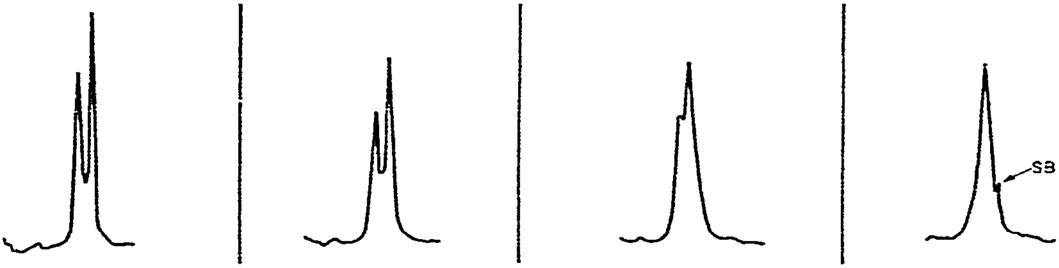
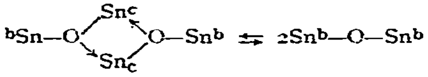


Fig. 2. Effect of temperature on proton NMR of (I). From left to right: 55°, 65°, 75°, 85°.

higher temperatures. When the molecule dissociates the concentration of (c) protons decreases, and as required by this argument, the (b) peak increases. The reaction (1) is:



(1)

The changes in chemical shift with temperature listed in Table 3 are small [0.03 ppm downfield shift in the (b) peaks for a temperature change from 40° to 85°]. We feel that this relatively minor shift is to be expected since only the monomer exists at higher temperatures. Strictly speaking, the peaks in the monomer should be downfield from the (b) peaks of the dimer. This is a consequence of the fact that the tin atoms of monomer are slightly less shielded than the tin atoms of the dimer which carry the b methyls. This deshielding in the dimer is the result of the oxygen donating some of its electrons to the coordinate bond. Because of the separation of the oxygen and the (b) protons the effect, and the shift, should be small. Application of this approach would also lead to the prediction that the (c) protons should occur at lower field than the (b) protons in complete agreement with the assignment above.

TABLE 3

VARIATION OF δ WITH TEMPERATURE

Temp. (°C)	δ_b (ppm)	δ_c (ppm)
~40	0.54	0.63
55	0.54	0.64
65	0.55	0.63
75	0.56	0.63
85	0.57	—

TABLE 4

THERMODYNAMIC DATA

T (°C)	K	σK	ΔF (kcal/mole)
20.0	0.470	0.124	0.4_4
31.5	0.586	0.230	0.3_2
37.0	0.972	0.182	0.1_1
49.0	1.960	0.098	-0.4_3

If the area under the portion of the curves, due to the (b) and (c) protons respectively, are B and C, then the equilibrium constant for reaction (1) is given by:

$$K = \frac{(B-C)^2}{C}$$

From values of K determined at several temperatures (Table 4) the ΔH for reaction (1) was calculated by the Van 't Hoff equation*. A least-square treatment of the data in Table 4 gives a value of 9 ± 1 kcal/mole for ΔH. Values of ΔF were also calculated and are included in Table 4.

The value for ΔH is given to only one significant figure. Because the two peaks were not completely separated, integration of the curves presented some difficulties. We estimate that an uncertainty of at least ± 1 kcal/mole is associated with the value for ΔH.

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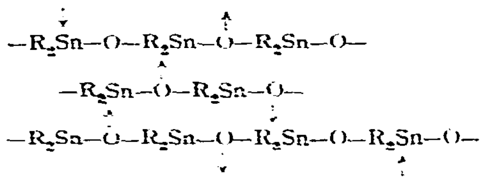
* $$\frac{\mathrm{d} \ln K}{\mathrm{d}T} = -\frac{\Delta H}{RT^2}$$

DISCUSSION

The weakly positive values for the ΔF of the dissociation process, changing over to a negative value at the higher temperature, as well at the positive values of ΔS (29 e.u.), are as would be expected. Since two coordinate bonds are ruptured in the dedimerization the value of 9 ± 1 kcal/mole for ΔH gives a value of 4.5 kcal/mole, making the assumptions usual in this type of treatment[6], for the dissociation energy of the tin–oxygen coordinate bond. This value compares with the ΔH (aq.) for the silver ion–cyclohexane complex of 6 kcal/mole[7] measured at 25°, or the bond energy of 5.30 kcal/mole[8] for each hydrogen bond in the acetic acid dimer determined in carbon tetrachloride at ambient temperatures.

One of the interesting points of Group IV chemistry is an explanation for the complete difference in properties between the silicones and the infusible, insoluble poly(disubstituted organotin oxides). Reichle[9] and Poller[10] have ascribed this to the formation of cross-links involving tin and oxygen atoms in different chains. The distannoxane (I), and its analogues, are models for the poly(disubstituted organotin oxides) (II).



(II)

The coordinate bonds holding the ring of (I) together are the mechanism for cross-linking and it would not take too many such bonds, even with a dissociation energy of only 4.5 kcal/mole, to convert a linear oxide into an infusible insoluble gel.

SUMMARY

The structure of tetramethyl-1,3-bis(trimethylsiloxy)distannoxane is known from X-ray analysis. The proton magnetic resonance spectra of this compound demonstrates that its dimeric nature is preserved in solution. It is possible to make assignments for all the chemical shifts and coupling constants involving protons. The temperature dependence of the spectra shows that the dimer dissociates in solution. From the equilibrium constants obtained at several temperatures the strength of the tin–oxygen coordinate bond is estimated.

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