Preliminary communication

# CARBON-13 NMR STUDIES OF EXCHANGE IN $R_3SnER'_n$ DERIVATIVES

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Summary

Carbon-13 NMR data are reported for trimethyltin derivatives containing $ER_n$ groups where E = C, Si, Ge, Sn, N, O and S including a series of cyclic amines with ring sizes from three to seven. Coupling constant values for the homologous series of fourth group derivatives give good correlations with the electronegativity of E. The observation of the two-bond, $| {}^2J({}^{119}Sn—E—{}^{13}C) |$ couplings only in the derivatives containing bulky R groups is rationalized by a bimolecular exchange of $ER_n$ groups in the concentrated solutions studied.

Three-bond, $| {}^3J({}^{119}Sn—N—C—{}^1H) |$ couplings in stannylamines (ca. 40 Hz) have been used to study exchange processes involving breakage of the Sn—N bond [1]. We now extend these studies to the two-bond, $| {}^2J({}^{119}Sn—E—{}^{13}C) |$ couplings to carbon-13 in $(CH_3)_3SnER_n$ systems for some of which exchange is possible.

The data for the organotin compounds measured appear in Table 1. NMR parameters were obtained on a modified Varian HA-100D spectrometer operating at 25.14 MHz in the Fourier transform mode as described previously [2]. Data for compounds I [3, 4] and XVI [5], included for comparison purposes, were taken from the literature. Scattered reports of data for compounds II [6], IV [5,7], XVII [5], XVIII [8,9] and XI [8] agree with our determination within experimental error. Assignments of carbon resonances were based upon multiplicities arising in the $^1H$ undecoupled spectra, the large magnitude of $| {}^1J({}^{119}Sn—{}^{13}C) |$ and data for related organotin compounds [2, 3].

*Chemical shifts.* When E is a fourth group atom the shieldings of the methyltin carbon atoms [$\delta({}^{13}CH_3Sn)$] are substantially greater than when E is an atom of higher electronegativity. Within the homologous series of compounds I-IV, however, correlations of either $\delta({}^{13}CH_3Sn)$ or $\delta(E{}^{13}CH_3)$ with electronegativity
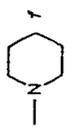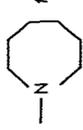
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TABLE 1

CARBON-13 NMR DATA FOR $(CH_3)_3SnER_n$ DERIVATIVES [a]

| Compound | $ER_n$ | $\lvert^1J(^{119}Sn-^{13}CH_3)\rvert$ (Hz) | $\lvert^2J(^{119}Sn-E-^{13}C)\rvert$ (Hz) | $\delta(^{13}CH_3)$ (ppm) | $\delta(E-^{13}C)$ (ppm) |
|---|---|---|---|---|---|
| I [b] | $C(CH_3)_3$ | 295.7 | 56.0 [c] | −12.20 | +29.90 |
| II | $Si(CH_3)_3$ | 245.8 | 60.1 | −12.28 | +0.52 |
| III | $Ge(CH_3)_3$ | 255.1 | 56.4 | −11.56 | −0.36 |
| IV | $Sn(CH_3)_3$ | 244.9 | 56.9 | −10.21 | −10.21 |
| V | $N(CH_3)_2$ | 381.2 | — | −8.67 | 43.43 |
| VI [d] | $N(CH_2CH_3)_2$ | 378.8 | 7.0 | −6.72 | 46.52 |
| VII [e] | $N[(CH_2)_3CH_3]_2$ | 381.0 | 7.2 | −6.80 | 52.78 |
| VIII |  | 374.4 | | −8.2 | 21.0 |
| IX |  | 372.0 | | −6.6 | 21.5 [g] |
| X |  | 378.0 | | −7.2 | 40.7 [h] |
| XI |  | 382.0 | | −8.3 | 54.2 |

| Compound | Substituent | | | | |
|---|---|---|---|---|---|
| XII | (pyrrolidine ring) | 380.8 | | −8.5 | 51.2 |
| XIII | (piperidine ring) | 378.6 | 10.0 | −8.2 | 52.1 |
| XIV | (azocane ring) | 382.2 | 10.6 | −7.3 | 54.5 |
| XV[i] | OCH₃ | 398.0 | k | −5.72 | 52.84 |
| XVI[j] | OC₂H₅ | 416.0 | | −3.1 | 58.1 |
| XVII | SCH₃ | 355.8 | | −6.01 | 8.54 |
| XVIII[l] | SCH₂CH₃ | 354.1 | 15.6 | −5.50 | 21.00 |

[a] Coupling constants, ±0.25 Hz; chemical shifts, ±0.03 ppm relative to internal TMS. Negative shifts are shielded relative to TMS. [b] Saturated solution in CCl₄. Data were taken from ref. 3. [c] From ref. 4. [d] δ(CH₃) 17.48 ppm; |³J(¹¹⁹Sn—N—C—¹³CH₃)| 13.2 Hz. [e] δ (N—C—¹³CH₂) 34.48, δ (N—C—C—¹³CH₂) 20.50, δ(¹³CH₂) 14.32 ppm; |³J(¹¹⁹Sn—N—C—¹³CH₂)| 22.5 Hz, ⁴J, ⁵J were not detected. [f] Values determined from 50% v/v solutions in benzene-d₆. [g] The remaining two resonances at 27.9 and 29.2 ppm cannot be assigned with certainty. [h] The remaining resonances centered near 56.5 ppm cannot be assigned with certainty. [i] Saturated solution in CDCl₃. [j] Data were taken from ref. 5. [k] Not reported. [l] δ(CH₃) 20.38 ppm; |³J(¹¹⁹Sn—S—C—¹³CH₃)| 16.4 Hz.

are poor (correlation coefficients less than 0.5). Similar unsatisfactory correlations are observed with the methyl—carbon chemical shifts in the fourth group thiophenoles, $C_6H_5SE(CH_3)_3$, where E = C, Si, Ge, Sn and Pb [10]. Calculation of shielding parameters for the trimethyltin moiety by comparison of the chemical shifts for the derivatives in Table 1 with data for the corresponding parent alcohols, thiols and amines is unjustified owing to solvation and hydrogen bonding effects which influence these shifts.

*Coupling constants.* In the homologous series of compounds I-IV, values of $|{}^1J({}^{119}Sn—{}^{13}CH_3)|$ correlate well with the Allred—Rochow electronegativity [11] of E (correlation coefficient 0.996). The value of $|{}^2J({}^{119}Sn—C—{}^{13}CH_3)|$ for I of < 1 Hz was corroborated by the authors of references 3 and 4 but the remaining three values of $|{}^2J({}^{119}Sn—E—{}^{13}CH_3)|$ which we recorded also correlate reasonably well with the electronegativity of silicon, germanium and tin.

No tin satellites were observed on the N-methyl proton resonances of neat trimethyl(dimethylamino)stannane [1], or on the singlet methylene bridge proton resonance of N-trimethyltin aziridine in concentrated solution [12], each to −50°C. The aziridine derivative is dimeric in solution [12], and associated

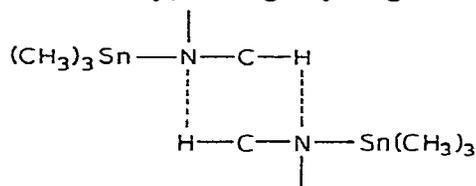species such as  have been postulated as intermediates in the bi-

molecular exchange of amino groups in neat liquid stannylamines which involves the breaking of the Sn—N bond, and consequent decoupling of the NMR $|{}^3J({}^{119}Sn—N—C—{}^1H)|$ in the rapid exchange limit. These couplings are, however, present in the ambient temperature proton spectra of the diethylamino derivatives, and the tin satellites of the N-methyl proton resonance in triethyl(dimethylamino) stannane coalesce at 90°C and can no longer be detected at 130°C [1].

Examination of Table 1 reveals that two-bond, $|{}^2J({}^{119}Sn—E—{}^{13}C)|$ couplings are resolved in the amine series only in ring derivatives containing more than five members, or in the straight chain amines, only in the diethyl or dibutyl derivatives. Two-bond, silicon-29 couplings have also been observed in bis[N,N-bis(trimethylsilyl)amino]tin(II) [13] in which a bulky group is present. The magnitude of the two-bond, $|{}^2J({}^{119}Sn—N—{}^{13}C)|$ (7.0-10.6) or $|{}^2J({}^{119}Sn—S—{}^{13}C)|$ (15.6 Hz) is clearly large enough to be detected in the other cases since the linewidths are ≤ 3.0 Hz at their largest (2.0 for the dimethylamino and 2.5 Hz for the methylsulfide derivatives, respectively), yet no tin satellites are resolved for the dimethylamino or small-ring nitrogen derivatives, or for the methylsulfide, or for either of the alkoxides studied in concentrated solution to −50°C.

Recently Van der Berghe and Van der Kelen have detected the proton $|{}^3J({}^{119}Sn—N—C—{}^1|H)|$ couplings in dilute solutions of the dimethylaminostannanes in which the postulated bimolecular exchange processes [1] would be ex-

pected to be slower, but these workers rejected the exchange postulate for one involving line broadening arising from interaction of the observed proton with the quadrupolar nitrogen-14 atom. The interaction was said to take place intermolecularly, through hydrogen bridges in concentrated solution [14]:

$$
\begin{array}{c}
| \\
(CH_3)_3 Sn \longrightarrow N \longrightarrow C \longrightarrow H \\
\vdots \qquad | \\
\vdots \qquad | \\
H \longrightarrow C \longrightarrow N \longrightarrow Sn(CH_3)_3 \\
|
\end{array}
$$

Their hypothesis also calls for association in a bimolecular process, but replaces the exchange postulate with hydrogen bonding, and rationalizes the disappearance of the tin satellites on their being lost in quadrupolar line broadening.

The exchange of amino groups at tin is of course the basis for the synthetically useful transamination method [15-16], which is generally thought to proceed through an $S_N2$ mechanism involving nucleophilic attack at tin [17]. The nitrogen to tin bridging found in the crystal structure of trimethyltin glycinate [18], and that suggested for N-trimethyltin aziridine by its dimeric nature in benzene, large Mössbauer quadrupole splitting (2.27 ± 0.12 mm/s) and basicity sufficient to remove $BF_3$ from its etherate [12], make the hydrogen bonding hypothesis [14] untenable. Indeed, we observe the same dependence upon steric bulk in the methyl- and ethyl-sulfides, but sulfur lacks a quadrupolar isotope in high natural abundance (sulfur-33; $I = 3/2$; 0.76%).

## Acknowledgement

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