*Journal of Organometallic Chemistry*, 148 (1978) 339—354

# $C^{13}$ N.M.R. SPECTROSCOPY ON BUTYLTIN COMPOUNDS CONTAINING N-, O- and S- LIGANDS.

by G. Domazetis, R.J. Magee and B.D. James,
Department of Inorganic and Analytical Chemistry,
La Trobe University, Bundoora, Vic. 3083, Australia.
(Received December 4th, 1977)

## SUMMARY

$^{13}C$ NMR data are reported for a range of tributyl and dibutyl-tin complexes containing O, N and S ligands. The coupling constant $J^1$ appears to be indicative of the coordination state of the tin atom. Using $J^1$, shift values and other supporting evidence, structures for a number of the compounds are proposed.

---

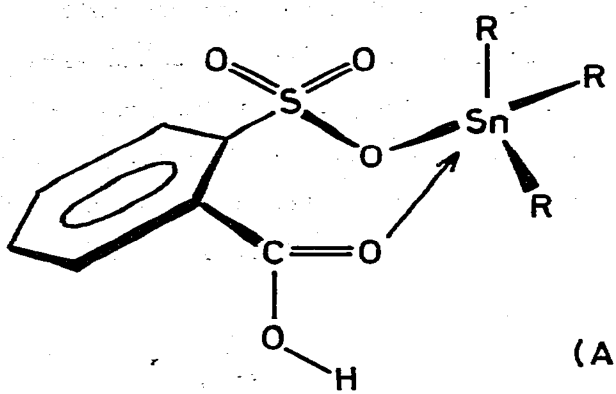
Carbon-13 N.M.R. spectroscopy has been shown to be a powerful tool for the study of organotin compounds[1-3]. It is generally accepted that the Fermi contact term is dominant for organometallics[1,3,4] and that the value of the coupling constant, may reflect the "amount of s character" in the Sn-C bond[5,6]. While caution should be exercised in the use of coupling constants[7], they are strongly indicative of the coordination state of the tin atom, and indeed such a classification has been made for a number of dialkyl- and trialkyl tin compounds[1].

We have prepared a range of compounds containing butyltin entities bonded to ligands containing oxygen, nitrogen and sulfur atoms in order to study the coordination states of tin, and the potential of each donor atom to coordinate to the metal. In view of the scarcity of $C^{13}$ N.M.R. data available on such systems, we present here tabulations of the appropriate parameters together with the implications of this data for some of the systems studied.

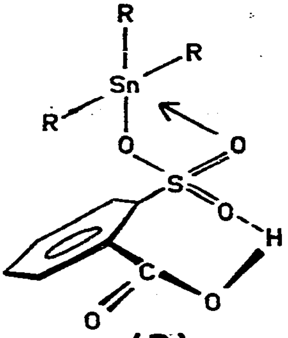
Tributyltin Compounds

Generally, $J^1$ ($Sn^{119/117} - C^{13}$) values for tributyltin compounds with coordination number four, decrease in the order O > Cl > S, indicating that Bent's rule is obeyed for these systems. Chemical shifts of carbon in the butyl groups vary significantly for the atom which is in the α-position with respect to tin, while the β, γ and δ values do not.

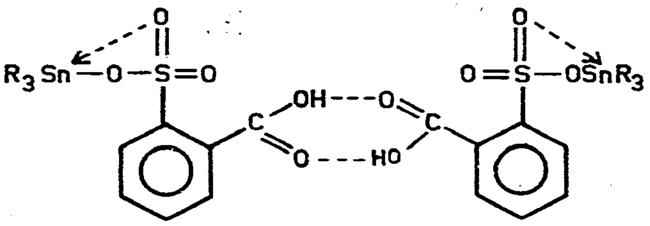
The tributylstannyl derivative of o-sulfobenzoic acid has a coupling constant, $J^1$ ($Sn^{119} - C^{13}$) of 400 Hz. This could indicate four coordination or distorted five coordination around the tin atom. The infrared spectrum contains a strong band at 1723 $cm^{-1}$, typical of the carboxyl group in benzoic acids, and a band at 2650 $cm^{-1}$ which is characteristic of hydrogen bonded carboxylates[18]. The $H^1$ N.M.R. spectrum contains a broad peak at 11.6 p.p.m., which can be attributed to a carboxylic acid proton. Although molecular models show that a structure such as (A) could readily form, the data rules out this possibility. In chloroform solution, the molecular weight of the complex is 602 which indicates that monomeric and dimeric species (such as B and C) are in equilibrium. The coupling constant value may be increased by a weak interaction between tin and another sulfonyl oxygen atom as indicated in the figures.



(A)

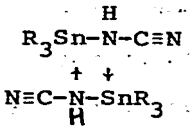


(B)



(C)

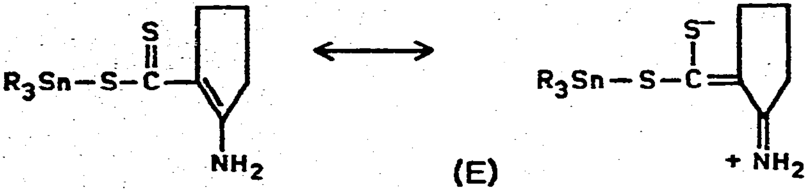
The compound N-(tributylstannyl)cyanimide, $(n\text{-}C_4H_9)_3SnNHCN$, is dimeric in benzene and the Mössbauer data suggests a coordination number greater than four[8]. Its $J^1$ value of 502 Hz is consistent with a five-coordinate structure, possibly of the type (D).



$$\begin{array}{c} \mathrm{R_3Sn{-}\overset{H}{N}{-}C{\equiv}N} \\ \uparrow\ \downarrow \\ \mathrm{N{\equiv}C{-}\underset{H}{N}{-}SnR_3} \end{array}$$

(D)

For S-(tributylstannyl),2-mercapto,5-nitropyridine and S-(tributylstannyl),2-amino cyclopentenedithiocarboxylic acid, both compounds display $J^1$ values of 350 Hz typical of 4-coordinate tin, thus indicating that the organic sulfur ligands are unidentate. In the case of the compound with the 2-aminocyclopentene dithiocarboxylate ligand, the α-C shift is 16.8 ppm which is somewhat higher than corresponding values for typical thiol derivatives. Resonance of the type (E) may account for the higher α-C shift value.

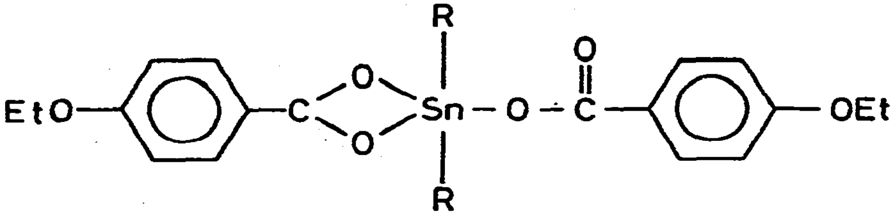


(E)

## Dibutyltin Compounds

Tin displaying coordination numbers of 4,5 or 6 are represented among the dibutyltin compounds. Only acetylacetone ($J^1$ = 910 Hz) and benzoylacetone ($J^1$ = 901 Hz) appear to force the tin into a six coordinate state. (Table 1). The molecular weight determinations[9] indicate that these complexes are monomeric in solution. The $J^1$ values are thus consistent with the infrared[10] and Mössbauer studies which indicated octahedral stereochemistry[11], with *trans* alkyl groups. Sulfur- and nitrogen- containing ligands usually favour structures with 5-coordinate tin. Other oxygen donors such as acetate, benzoate and alkoxy groups also seem to cause pentacoordination of the tin.

Dibutyltin bis(p-ethoxybenzoate) is monomeric in $CHCl_3$ and its $J^1$ value is 586 Hz. This is much lower than for the 6-coordinate compounds and is in the range expected for 5-coordinate tin. Although a structure such as (F) could be written, the carbonyl carbon shifts are equivalent (175.6 ppm), thus suggesting a rapid bidentate-unidentate interchange of the coordinating groups.



(F)

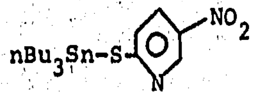
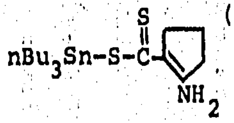
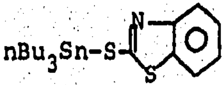
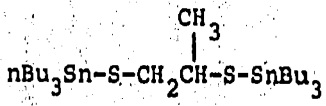
Similarly, the compound S-(dibutylstannyl)bis(2-mercaptobenzothiazole, also monomeric in $CHCl_3$, displays a $J^1$ value of 505 Hz, again characteristic of 5-coordinate tin. Thus, the structure (G) is postulated. Again, chelation interchange is possible and, in this case, the fifth interaction with the metal could be via either sulfur or nitrogen.

Reaction of dibutyltin oxide with ethylene glycol yields the ten-membered ring 1,1,6,6-tetra-n,-butyl-1,6-distanna-2,5,7,10-tetraoxyacyclodecane. Whilst this compound is monomeric in solution[12], the $J^1$ value (653 Hz) is again typical of 5-coordinate tin. A broad band at 400 $cm^{-1}$ in the infrared spectrum could be due to a O→Sn interaction[13]. Molecular models indicate that the structure (H) is favoured and that a rapid interchange of coordinating oxygens is possible. Such interchange would make the carbon atoms of

(Continued on p.347)

## TABLE 1

## $C^{13}$ N.M.R. DATA FOR THE ORGANOTIN MOIETY IN SOME BUTYLTIN COMPOUNDS

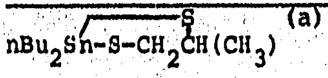
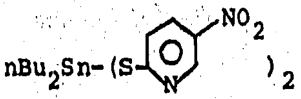
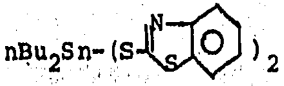
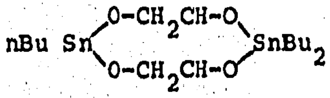
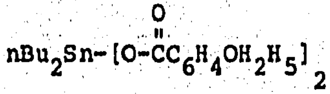
| Compound | δ(C)α | δ(C)β | δ(C)γ | δ(C)δ | $J^1$ | $J^2$ | $J^3$ |
|---|---|---|---|---|---|---|---|
| $nBu_4Sn$ (a) | 9.0 | 29.7 | 27.8 | 13.9 | 313 | – d | 54 |
| $nBu_3SnCl$ (a) | 17.2 | 27.5 | 26.4 | 13.7 | 341 | 46 | 67 |
| $nBu_3Sn-S(nC_4H_9)$ (a) | 13.0 | 28.7 | 27.1 | 13.5 | 330 | 26 | – |
| $nBu_3Sn-SC_6H_4-pCH_3$ (a) | 14.2 | 28.6 | 27.1 | 13.6 | 326 | 40 | 61 |
|  (b) | 15.8 | 28.8 | 27.1 | 13.6 | 350 | 22 | 52 |
|  (b) | 16.8 | 29.3 | 27.3 | 13.9 | 350 | 40 | 96 |
| $nBu_3Sn-NHCN$ (a) | 18.3 | 28.6 | 27.2 | 13.8 | 502 | 27 | 74 |
|  (a) | 16.4 | 28.8 | 27.0 | 13.7 | 336 | 22 | 62 |
|  $nBu_3Sn-S-CH_2CH(CH_3)-S-SnBu_3$ (a) | (20.7)<br>20.3 | (28.8)<br>28.4 | (27.2)<br>26.8 | 13.8 | – | – | – |

## TABLE 1 (Continued)

| Compound | δ(C)α | δ(C)β | δ(C)γ | δ(C)δ | $J^1$ | $J^2$ | $J^3$ |
|---|---|---|---|---|---|---|---|
| $nBu_3Sn-S-CH_2CH_2NH_2$ (b) | 17.8<br>15.8 | 28.6 | 27.1 | 13.6 | - | - | - |
| $nBu_3Sn-OCH_3$ (a) | 14.2 | 28.4 | 27.4 | 13.8 | 370 | 22 | 62 |
| $nBu_3Sn-O\ CH_2CH_2NH.nC_3H_7$ (a) | 14.8<br>16.5 | 28.4 | 27.5 | 13.8 | 360<br>370 | - | - |
| $nBu_3Sn-O\ CH_2CH_2NH.nC_4H_9$ (a) | 14.8<br>16.5 | 28.4 | 27.4 | 13.8 | 369<br>371 | $45^c$ | $105^c$ |
| $nBu_3Sn-O\ CH_2CH_2NH.nC_6H_{13}$ (a) | 14.7<br>16.5 | 28.4 | 27.4 | 13.8 | 367<br>(-) | - | - |
| $nBu_3-Sn-O\ CH_2CH_2NH.nC_8H_{17}$ (a) | 14.8<br>16.5 | 28.2 | 27.3 | 13.7 | 365<br>(-) | - | - |
| $nBu_3Sn-O\ CH_2C(CH_3)_2-NH_2$ (a) | 15.6 | 28.3 | 27.3 | 13.7 | 376 | - | 82 |
| $nBu_3Sn-O_3SC_6H_4COOH$ (b) | 20.3 | 27.8 | 26.9 | 13.7 | 406 | - | 74 |
| $nBu_2SnCl_2$ (b) | 27.1 | 27.1 | 26.3 | 13.6 | 402 | — | — |
| $nBu_2Sn-[S(n)Bu]_2$ (a) | 17.6 | 28.5 | 26.9 | 13.7 | 386 | 23 | - |

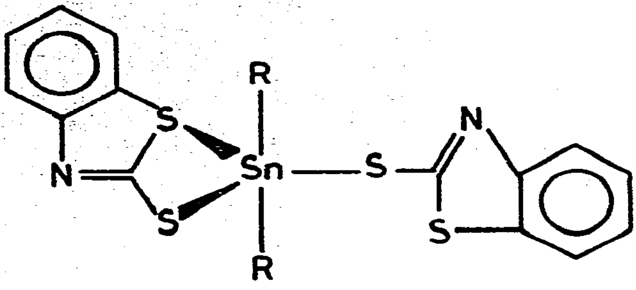
Contd...

TABLE 1 (Continued)

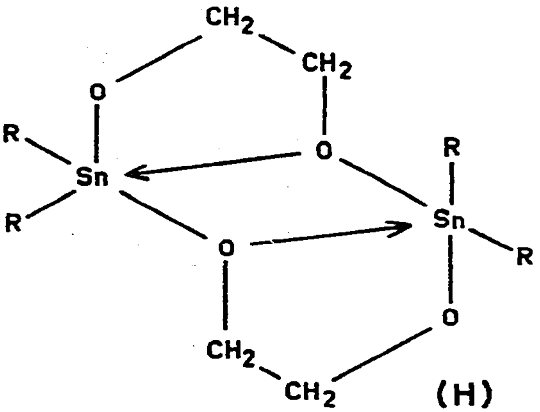
| Compound | δ(C)α | δ(C)β | δ(C)γ | δ(C)δ | $J^1$ e | $J^2$ | $J^3$ |
|---|---|---|---|---|---|---|---|
|  (a) | 20.7 | 28.2 | 26.5 | 13.5 | - | 27 | 70 |
| $nBu_2Sn-[SØpCH_3]_2$ (a) | 18.4 | 27.9 | 26.4 | 13.4 | 365 | 26 | - |
|  (b) | 26.4 | 28.4 | 26.4 | 13.6 | 523 | 34 |  |
| $nBu_2Sn[DTC(Benz)_2]_2$ (b) | 34.6 | 28.7 | 26.4 | 13.9 | 566 | 39 | - |
|  (b) | 28.9 | 28.2 | 26.3 | 13.7 | 505 | - | - |
| $nBu_2Sn(O_2CCH_3)_2$ (b) | 25.0 | 26.8 | 26.4 | 13.6 | 601 | - | - |
| $nBu_2Sn(Acac)_2$ (a) | 27.3 | 27.7 | 26.4 | 13.9 | 910 | 42 | 122 |
| $nBu_2Sn(Bzac)_2$ (a) | 27.9 | 27.3 | 26.4 | 13.8 | 901 | - | - |
|  (b) | 22.7 | 27.7 | 27.1 | 13.6 | 653 | 34 | 101 |
|  $nBu_2Sn-[O-\overset{O}{\overset{\Vert}{C}}C_6H_4OH_2H_5]_2$ (b) | 25.5 | 26.8 | 26.4 | 13.5 | 586 | 20 | 98 |

a - spectrum obtained from neat liquid. b - spectrum obtained from 50% $CDCl_3$ or saturated solutions c - estimated value. d - coupling constant cannot be estimated from data. e - $J^1$ values reported are for $Sn^{119} - C^{13}$.

the glycol ligand equivalent, and this is consistent with the $C^{13}$ N.M.R. data (Table 2).



(G)



(H)

## Chemical shifts of ligands

Table 2 contains information for some sulfur and oxygen ligands. The ligands that can readily be discussed are the thiols and the aminoalcohols. The thiols $\underline{n}C_3H_2S$- and $\underline{n}$-$C_4H_9S$- exhibit shifts similar to those of the $SR^-$ anion, while those of $CH_3$-$C_6H_4S$- are consistent with a substituted thiophenol where the substituent exerts an electron donating effect[14]. β effects of 0.5 and 1.2 ppm are shown for the -S-$C_4H_9$ derivatives of $(n\text{-}Bu)_3Sn$ and $(n\text{-}Bu)_2Sn$, respectively, indicating that the organotin groups

(Continued on p.350)

## TABLE 2

## SHIFT VALUES OF SOME LIGANDS

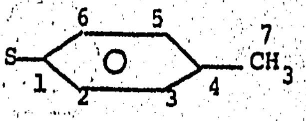
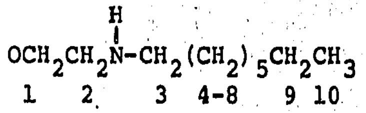
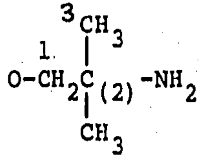
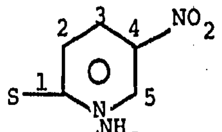
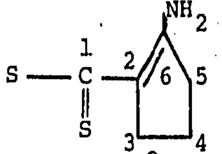
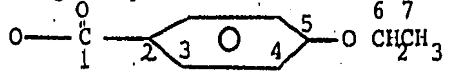
| Compound | Chemical Shift Rel.TMS ppm. for C atoms | | | | | | | Ligand |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| $nBu_3SnSR$ | 24.3 | 36.5 | 21.7 | 13.6 | | | | $S\text{-}\overset{1}{CH_2}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_3}$ |
| $nBu_2Sn(SR)_2$ | 26.9 | 36.8 | 21.9 | 13.7 | | | | $S\text{-}CH_2CH_2CH_2CH_3$ |
| $nBu_3Sn\text{-}SC_6H_4R$ | 131.0 | 129.2 | 134.7 | 135.2 | 134.7 | 129.2 | 20.9 |  |
| $nBu_2Sn(SC_6H_4R)_2$ | 134.7 | 129.2 | 134.7 | 135.2 | 134.7 | 129.2 | 20.8 | |
| $Bu_3Sn\text{-}SCH_2CH(CH_3)S\text{-}SnBu_3$ | 46.9 | 43.5 | 23.9 | | | | | $S\text{-}\underset{1}{\overset{\mid}{CH_2}}\text{—}\overset{\overset{3}{CH_3}}{\overset{2\mid}{CH}}\text{-}S$ |
| $nBu_3SnOCH_2CH_2NHR$ | 65.2*<br>(54.3) | 57.5<br>(54.3) | 52.2<br>21.6 | 23.8 | 11.9 | | | $O\text{-}\overset{1}{CH_2}\text{-}\overset{2}{CH_2}\text{-}\overset{H}{\overset{\mid}{N}}\text{-}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_3}$ |
| | 65.4 | 54.8<br>(55.3) | 50.1 | 32.9 | 22.6 | 14.0 | | $-O\text{-}\overset{1}{CH_2}\overset{2}{CH_2}\overset{H}{\overset{\mid}{N}}\text{-}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$ |
| | 65.3<br>13.7(C8) | 54.7 | 50.4 | 32.3 | 30.7 | 23.0 | 13.9 | $-O\underset{1}{CH_2}\underset{2}{CH_2}\overset{H}{\overset{\mid}{N}}\text{-}\underset{3}{CH_2}\underset{4}{CH_2}\underset{5}{CH_2}\underset{6}{CH_2}\underset{7}{CH_2}\underset{8}{CH_3}$ |

TABLE 2 (Continued)

| Compound | Chemical Shift Rel.TMS ppm. for C atoms | | | | | | | Ligand |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| | 65.2 | 54.3 | 50.3 | 32.0 | 30.5 | 29.8 | 29.5 | <br>$\overset{1}{OCH_2}\overset{2}{CH_2}\overset{H}{N}-\overset{3}{CH_2}\overset{4-8}{(CH_2)_5}\overset{9}{CH_2}\overset{10}{CH_3}$ |
| | 27.6 (C8), 22.7 (C9), 13.8 (C10) | | | | | | | |
| $nBu_3SnOCH_2C(CH_3)_2NH_2$ | 73.5 | 51.3 | 8.9 | | | | | <br>$O-\overset{1}{CH_2}C_{(2)}(\overset{3}{CH_3})(CH_3)-NH_2$ |
| $nBu_2SnSC_5H_3N.NO_2$ | 140.6 | 124.3 | 130.3 | 151.3 | 143.8 | | |  |
| $nBu_2Sn(SC_5H_3N.NO_2)_2$ | 141.0 | 124.6 | 131.4 | 158.4 | 142.8 | | | |
| $nBu_3SnS_2C.C_5H_6NH_2$ | 206.1 | 167.4 | 37.2 | 19.8 | 36.1 | 120.6 | |  |
| $nBu_2Sn(OC.OC_6H_4OEt)_2$ | 175.6 | 122.8 | 132.5 | 114.0 | 162.9 | 63.7 | 14.7 |  |
| $(nBu_2Sn)_2(OCH_2CH_2O)_2$ | 63.2 | | | | | | | $-O-CH_2CH_2-O-$ |

---

*The N-propyl derivative displays marked non-equivalence for the C atoms labelled 2, 3 and 4. The 54.3 ppm peak may be associated with either C2 or C3.

exert different steric effects. The α-carbon of the thiol is β to tin, and the higher shift value compared with the n-$C_4H_9S^-$ anion may indicate a steric influence. The compound $(n\text{-}C_4H_9)_3Sn\ SCH_2CH(CH_3)SSn(n\text{-}C_4H_9)_3$ exhibits non-equivalent α, β, and γ shift values for the tributyltin moieties. This presumably indicates that the $-CH(CH_3)-$ group exerts a pronounced steric influence on the organotin.

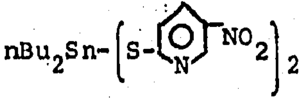
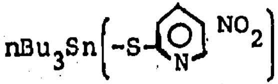
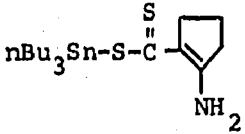
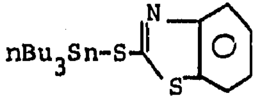
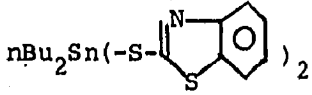
The tributyltin aminoalcohol compounds exhibit unique shift values that can be compared to the free ligand in only a limited way. The non-equivalence of carbons is observed in both the butyltin and the ligand moieties. The N-n-propyl derivative contains non-equivalent 2, 3, and 4, carbons, while the N-n-butyl derivative contains 2, 3, carbons that show non-equivalence. Steric factors are thought to be responsible for this: the smaller propyl group exists in a more rigid form relative to the hexyl and octyl derivatives. Inductive effects would also influence the shift values of these derivatives to a greater extent than perhaps the bulkier groups.

## EXPERIMENTAL

The compounds containing the ligands of interest were prepared using modifications of procedures involving butyltin oxide and the protonated ligand (method A)[15], the organotin halide and the sodium salt of the ligand (method B)[16] or the organotin halide, protonated ligand and sodium hydroxide (method C)[17]. Microanalytical data (Australian Microanalytical Service, C.S.I.R.O., Melbourne) are given in Table 3 for new compounds.

$C^{13}$ N.M.R. spectra were recorded from neat liquids where possible, or from concentrated solutions in $CDCl_3$ with TMS as internal standard, using a JEOL-PFT-100FT spectrometer

## TABLE 3. ANALYTICAL DATA

| Compound | Prep. Method | %C[a] | %H[a] | Other[a] | Mol.Wt.[a,d] |
|---|---|---|---|---|---|
|  | A | 39.85 (39.78) | 4.34 (4.42) | 11.3 (11.8)[b] | 570 (543.03) |
|  | C | 46.25 (45.74) | 7.25 (6.73) | 6.9 (7.2)[b] | |
| $nBu_3Sn\text{-}S\text{-}CH_2CH(CH_3)S\text{-}Sn\ Bu_3$ | B | 46.58 (47.23) | 8.62 (8.75) | 8.6 (9.3)[b] | |
|  | B | 47.65 (48.21) | 8.28 (7.81) | | |
| $nBu_3Sn\text{-}OCH_2CH_2NH.nPropyl$ | B | 51.92 (52.07) | 9.80 (10.01) | 3.28 (3.57)[c] | |
| $nBu_3Sn\text{-}OCH_2CH_2NH.nOctyl$ | B | 56.23 (57.15) | 9.80 (10.68) | 2.3 (3.0)[c] | |
|  | A | 50.22 (50.03) | 6.92 (6.85) | 14.2 (14.1)[b] | |
|  | A | 46.46 (46.73) | 5.10 (4.63) | | 564 (565.17) |
| $nBu_3Sn\text{-}SO_3C_6H_4COOH$ | A | 46.38 (46.46) | 6.62 (6.56) | 6.3 (6.5)[b] | 602 (491.14) |

a - figures in parentheses are expected values.
b - analytical values for S.
c - analytical values for N.
d - precision limits ±20.

operating at 25.15 MHz, and coupled to a JEOL EC-100 data collection system. Chemical shifts are accurate to ±0.1 ppm, and coupling constants to ±2.3 Hz – except for spectra with peak overlapping, for which ±5 Hz accuracy is obtained. Coupling constants were usually obtained from between 1,000 and 12,000 pulses. Assignments are based on off-resonance decoupling whenever possible and also by the use of satellite peaks and comparisons with previously reported values for known compounds. Infrared spectra were obtained from KBr pressed disks using a Perkin-Elmer 457 instrument calibrated with polystyrene film. Molecular weights were determined from $CHCl_3$ solutions at 35°C with a Perkin-Elmer 115 vapor phase osmometer.

## ACKNOWLEDGEMENTS

G.D. acknowledges support from a Commonwealth of Australia Postgraduate Research Award.

## REFERENCES

1. T.N. Mitchell, J. Organometal. Chem., 59, 189, (1973).
2. T.N. Mitchell, Org. Magn. Res., 1, 610, (1975).
3. D.Doddrell, M.L. Bullpit, C.J. Moore, C.W. Fong, W. Kitching, W. Adcock and B.D. Gupta, Tetrahedron Letters, 9, 665 (1973).
4. I. Iwayanagi, T. Ibusuki and Y. Saito, J. Organometal. Chem., 128, 145, (1977).
5. Bertha de Poorter, J. Organometal. Chem., 128, 361, (1977).
6. G. Barbieri, R. Benassi and F. Taddei, J. Organometal. Chem., 129, 27, (1977).

7. Bertha de Poorter and M. Gielen, J. Organometal. Chem., 124, 161, (1977).

8. J.A. Feiccabrino, E.J. Kupchick, J. Organometal. Chem., 56, 167, (1973).

9. R.C. Mehrotra and V.D. Gupta, J. Organometal. Chem., 4, 237, (1965).

10. Y. Kawasaki, T. Tanaka, R. Okawara, Bull. Chem. Soc. Japan, 37, 903, (1964).

11. G.M. Bancroft and T.K. Sham, Can. J. Chem., 52, 1361, (1974).

12. Wm. J. Considine, J. Organometal. Chem., 5, 263, (1966).

13. D.H. Lohman, J. Organometal. Chem., 4, 382, (1965).

14. G. Barbarella, P. Dembech, A. Garbesi, A. Fara, Org. Magn. Res., 8, 108 (1976).

15. G.S. Sasin, J. Org. Chem., 18, 1142 (1953).

16. R.C. Poller, J.A. Spillman, J. Chem. Soc., (A), 958, (1966).

17. E.W. Abel, D.B. Brady, J. Chem. Soc., 1192, (1965).

18. J.R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", p.46, Prentice-Hall (1965).