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# Bis(tributyltin) oxide as a wood preservative: its conversion to tributyltin carboxylates in *Pinus sylvestris*

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**Tributyltin compounds have been successfully used for many years as wood preservatives, although their chemical nature in timber has not been fully elucidated. This study by $^{119}$Sn and $^{13}$C NMR spectroscopy has shown that, on impregnation into *Pinus sylvestris* sapwood, bis(tributyltin) oxide [$(Bu_3Sn)_2O$] is rapidly converted to tributyltin carboxylates ($Bu_3SnOCO\cdot R$) via reaction with components of the wood resin. It is further suggested that the formation of these species is a prerequisite for the known disproportionation reaction which occurs in $(Bu_3Sn)_2O$-treated timber.**

Keywords: Tributyltin, wood preservative, structure, *Pinus sylvestris*

## INTRODUCTION

Tributyltin compounds, in particular bis(tributyltin) oxide [$(Bu_3Sn)_2O$], have been successfully used for many years as fungicides in organic solvent-based wood preservatives.[1,2] It has been reported, however, that the triorganotin compound undergoes dealkylation in timber[3] and that the total tin content in timber decreases with time.[4] Previously, we have demonstrated[5] that on impregnation into *Pinus sylvestris* (Scots pine), bis(tributyltin) oxide is rapidly converted to other tributyltin species, $Bu_3SnOX$, and that these subsequently undergo disproportionation to tetrabutyltin ($Bu_4Sn$) and $Bu_2Sn(OX)_2$ derivatives. We have additionally demonstrated that the $Bu_4Sn$, so produced is not persistent in timber and is lost by volatilization.

Herein, we report the results of an investigation by $^{119}$Sn and $^{13}$C NMR spectroscopy to elucidate the nature of the X moiety of the $Bu_3SnOX$ species formed in *P. sylvestris* sapwood.

## EXPERIMENTAL

Bis(tributyltin) oxide, $(Bu_3Sn)_2O$, was obtained from Schering AG, FRG, and was used without further purification.

Tributyltin linoleate was a gift from Witton Chemical Co. Ltd, Mildenhall, Suffolk, UK. The linoleic acid from which this was prepared was of 70% purity and contained unspecified amounts of linolenic and oleic acids.[6] Other tributyltin carboxylates were prepared according to previously published procedures.[7]

### Treatment of wood blocks

Twenty blocks of *P. sylvestris* sapwood (30mm × 10mm × 5mm) were vacuum-impregnated with a solution (2.0%, w/w) of $(Bu_3Sn)_2O$ in petroleum ether (b.p. 60–80°C) as described previously.[8] After 24 h, the blocks were Soxhlet-extracted for 48 h in 200 cm$^3$ benzene. The resultant solution was concentrated to approximately 3 cm$^3$ prior to NMR investigation. This overall procedure was repeated twice in order to check the consistency of results.

### NMR spectroscopy

$^{119}$Sn and $^{13}$C NMR spectra were recorded on a JEOL FX60Q instrument. Field frequency lock was to external $D_2O$. $^{119}$Sn spectra were measured under nuclear Overhauser suppressed conditions: chemical shifts ($\delta\,^{119}$Sn) are relative to $Me_4Sn$ and are accurate to ±0.5 ppm. $^{13}$C chemical shifts ($\delta\,^{13}$C) are relative

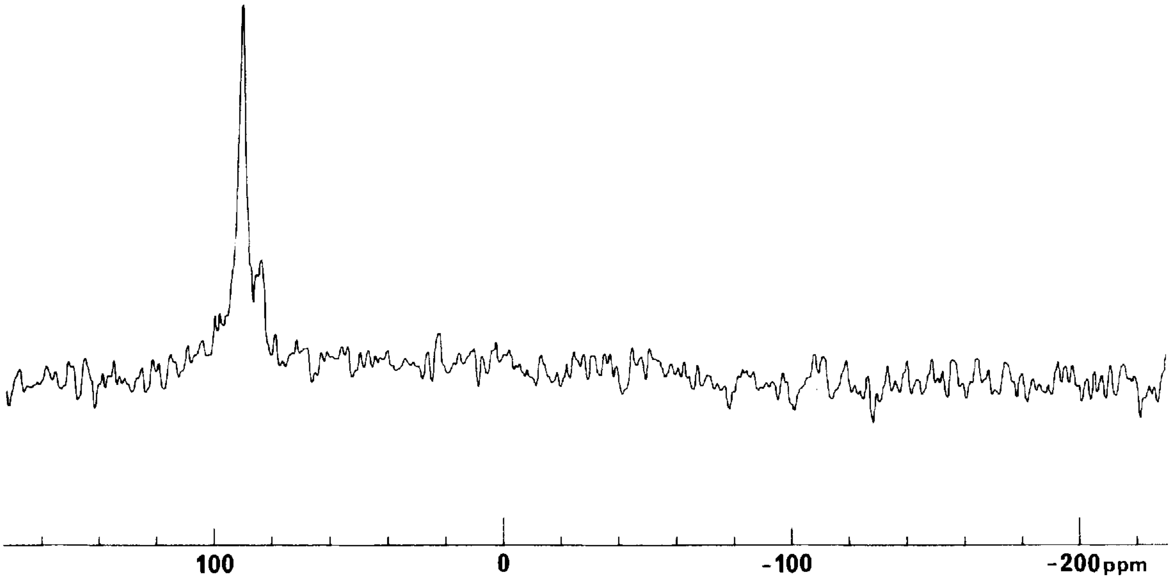


Figure 1 $^{119}$Sn NMR spectrum of a benzene extract solution of $(Bu_3Sn)_2O$-treated *P. sylvestris* sapwood blocks, obtained 24 h after treatment.

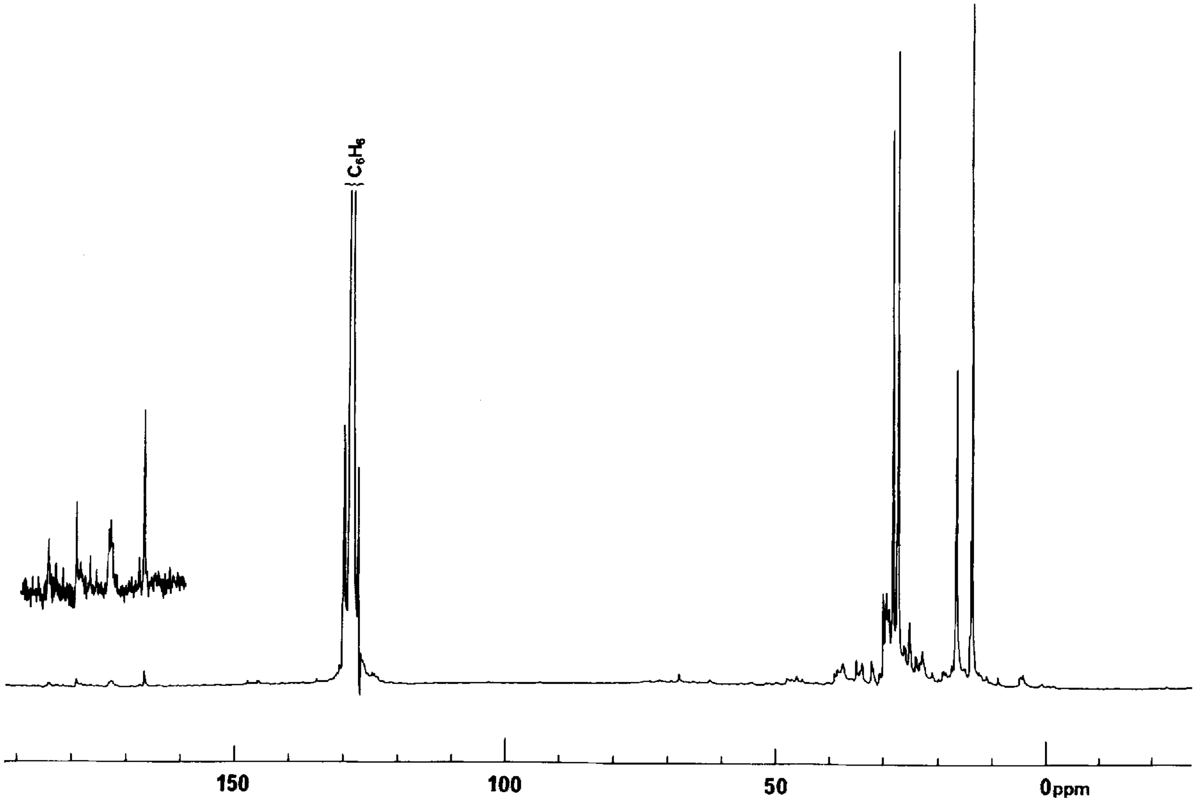
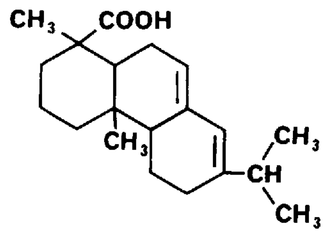


Figure 2 $^{13}$C NMR spectrum of a benzene extract solution of $(Bu_3Sn)_2O$-treated *P. sylvestris* sapwood blocks, obtained 24 h after treatment.


(I)

$CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7COOH$

(II)

to $Me_4Si$ and are accurate to ±0.1 ppm; coupling constants, $^1J(^{13}C-^{119}Sn)$, are accurate to ±1 Hz.

## RESULTS AND DISCUSSION

Figure 1 shows a typical $^{119}Sn$ NMR spectrum of a benzene extract of *P. sylvestris* sapwood, 24 h after impregnation with $(Bu_3Sn)_2O$. A broad asymmetric peak (line width approximately 60 Hz) is observed, centred at approximately 91 ppm, together with minor resonances at approximately 84, 99 and 106 ppm. Whilst there may be some doubt over the validity of the minor resonances due to the low signal to noise ratio, these peaks were consistently observed in both the present and previous work[5] and so are believed to be real. Furthermore, Fig. 1 shows a spectral range down to −200ppm, since any dibutyltin species, $Bu_2Sn(OX)_2$, extracted from timber will be observed at approximately −150ppm.[5] Bis(tributyltin) oxide in benzene (100 mg $cm^{-3}$) affords a single sharp resonance (line width approximately 7 Hz) at 84.1 ppm. Consequently, although some evidence of $(Bu_3Sn)_2O$ is seen in the spectra of the extract solutions, it is apparent that treatment of the wood blocks results in a change in the chemical nature of most of the organotin. Indeed, a $^{119}Sn$ chemical shift of 91 ppm is consistent with $Bu_3SnOX$ species. A similar change in the nature of $(Bu_3Sn)_2O$ in *P. radiata* has been reported elsewhere.[9]

Chemically, timber consists of three major components, cellulose, hemicellulose and lignin.[10] Each of these contains carbon-to-hydroxo (C–OH) groups and so could react with $(Bu_3Sn)_2O$ to form tributyltin alkoxides or phenoxides, which generally have $\delta^{119}Sn$ values in the range 80–110 ppm.[11] In addition, there are small amounts of resin in timber (typically a few per cent) which contain a variety of carboxylic acids.[12] The range of different acids present in wood resin is ill-defined and specific data for *P. sylvestris* sapwood, to our knowledge, is limited.[13] However, in general two types of acid have been identified.[12] These are the resin acids which may be exemplified by abietic acid (**I**) and both saturated and unsaturated fatty acids, of which linoleic acid (**II**) is often most abundant in *Pinus* species.[12] These acids could also react with $(Bu_3Sn)_2O$ to form tributyltin esters, which generally exhibit $\delta^{119}Sn$ values in the range 85–95 ppm.[11] Therefore, on the basis of $^{119}Sn$ NMR spectroscopy alone it is not possible to define the precise nature of the organotin compounds extracted from timber.

In order to gain further insight into the nature of these organotins, the $^{13}C$ NMR spectra of the extracted solutions were recorded and an example is shown in Fig. 2. The most intense peaks in these spectra are those expected for the butyl groups of tributyltin compounds and are at 28.4 (C-2), 27.4 (C-3), 16.7 (C-1) and 13.9 (C-4) ppm. Associated with the C-1 resonance are satellites arising from coupling to $^{117/119}Sn$. The magnitude of the $^1J(^{13}C-^{119}Sn)$ interaction is 368 Hz. The other main features of these spectra ranged from 14–40 ppm and are due to aliphatic $—CH_2—$ or $—CH_3$ groups. In addition, resonances due to carboxylate carbonyl groups, —CO·O—, are seen at 184.2, 179.0, 176.4, 172.6 and 166.5 ppm.

These observations preclude the bulk of the organotin in the extract solutions being present as tributyltin derivatives of carbohydrates or lignin, since these would show clear evidence of —CH—O— or —C(aromatic) resonances respectively at 60–100 and 120–150 ppm, yet only weak resonances are observed in these parts of the spectra. It is therefore likely that the organotins present are predominantly a mixture of tributyltin carboxylates, although the minor peaks at 99 and 106 ppm in the $^{119}Sn$ spectrum may possibly be due to small amounts of tributyltin alkoxides/phenoxides.

In order to test this observation the $^{119}Sn$ and $^{13}C$ NMR spectra of a number of tributyltin carboxylates, $Bu_3SnOCO{\cdot}R$ ($R{=}H$, $CH_3$, $CH_2CH_3$, $(CH_2)_2CH_3$, $(CH_2)_{10}CH_3$, $(CH_2)_{16}CH_3$, linoleyl and abietyl) were recorded (Table 1). It was found that, with one exception, the $\delta^{119}Sn$ values of the tributyltin

**Table 1** $^{119}$Sn and $^{13}$C parameters for tributyltin carboxylates, $Bu_3SnOCO{\cdot}R$[a]

| R | $\delta^{119}$Sn (ppm) | $\delta^{13}$C (ppm)[b] Butyl | | | | | | $^1J(^{13}C-^{119}Sn)$ (Hz) |
|---|---|---|---|---|---|---|---|---|
| | | C-1 | C-2 | C-3 | C-4 | C=O | R | |
| H | ~42 | 17.9 | 28.4 | 27.4 | 13.8 | 167.4 | | 416 |
| $CH_3$ | 92.4 | 16.4 | 28.1 | 27.2 | 13.7 | 176.3 | 21.0 | 364 |
| $CH_2CH_3$ | 92.0 | 16.4 | 28.1 | 27.2 | 13.7 | 179.5 | 28.1, 10.3 | 364 |
| $(CH_2)_2CH_3$ | 91.9 | 16.4 | 28.1 | 27.2 | 13.7 | 178.7 | 36.7, 19.5, 13.7 | 366 |
| $(CH_2)_{10}CH_3$ | 91.2 | 16.5 | 28.2 | 27.3 | 13.7 | 179.0 | 35.0, 32.6, 29.9(×3), 29.7(×3), 26.2, 23.0, 14.2 | 364 |
| $(CH_2)_{16}CH_3$ | 91.2 | 16.5 | 28.3 | 27.4 | 13.8 | 179.0 | 35.1, 32.3, 30.1(×8), 29.8(×4), 26.3, 23.1, 14.3 | 364 |
| Linoleyl[d] | 87.8 | 16.7 | 28.3 | 27.3 | 13.8 | 179.1 | | 368 |
| Abietyl[e] | 88.6 | 16.9 | 28.3 | 27.3 | 13.8 | 184.5 | 144.2, 136.0, 123.8, 121.3, 51.4, 46.9, 46.0 38.9, 38.6, 35.3, 34.9, 27.7, 26.5, 22.9, 21.6, 21.1, 18.8, 18.0, 14.3 | 362 |

[a] Spectra recorded in benzene solution (50 mg cm$^{-3}$). For composition of solution, see Table 2. [b] Unassigned resonances. Number of overlapping resonances is defined, where appropriate, in parentheses. [c] Resonances not reported due to impurity of sample — see Experimental Section. [d] Linoleic acid, $CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7COOH$. [e] Abietic acid, $C_{19}H_{29}COOH$: for structure see standard sources.

**Table 2** Components of tributyltin carboxylate, $Bu_3SnOCO{\cdot}R$, solution prepared for $^{119}$Sn and $^{13}$C NMR spectra (Table 1)

| R | Concentration (mol dm$^{-3}$ × 10$^{-4}$ in $C_6H_6$) |
|---|---|
| H | 2[a] |
| $CH_3$ | 1 |
| $CH_2CH_3$ | 1 |
| $(CH_2)_2CH_3$ | 1 |
| $(CH_2)_{10}CH_3$ | 1 |
| $(CH_2)_{16}CH_3$ | 1 |
| Linoleyl[d] | 4[b] |
| Abietyl[d] | 4[c] |

[a] Concentration based on relative intensities of —C=O resonances in Fig. 2. [b] Higher concentration, due to the probable predominance of linoleic acid in *Pinus* species — see text. [c] Higher concentration, since abietic acid is used to represent all the resin acids. [d] See footnotes to Table 1.

carboxylates are, as expected, in the region observed for the extract solution (Fig. 1). In the $^{13}$C spectra (Table 1), the magnitude of the $^1J(^{13}C-^{119}Sn)$ couplings, position of —CO·O— resonances and main aliphatic $—CH_2—$ peaks all suggest that these or similar compounds are present in the extract. With regard to $Bu_3SnOCO{\cdot}H$ the $\delta^{119}$Sn value is very different from those of the other tributyltin analogues. This lower-frequency chemical shift indicates[11] that even at a concentration of only 50 mg cm$^{-3}$ the tin atom has a five-coordinate geometry, presumably arising from C=O → Sn intermolecular association. The larger $^1J(^{13}C-^{119}Sn)$ value of 416 Hz in the $^{13}$C spectrum is in line with this structure, being consistent[14] with the expected increase in *s*-electron density in the tin—carbon (Sn—C) bonds in the associated species compared with a four-coordinate monomer.

As stated previously, wood resin contains a variety of carboxylic acids. Therefore, in order to obtain a closer comparison to the spectra of the extract (Figs 1 and 2), a solution containing a mixture of tributyltin compounds (as described in Table 2) was prepared and its $^{119}$Sn and $^{13}$C NMR spectra recorded (Figs 3 and 4). It can be seen from the $^{119}$Sn spectrum that this solution gives rise to a single peak centred at 90.9 ppm. With regard to the $^{13}$C spectrum, a single set of resonances attributable to the butyl groups is seen at 28.3 (C-2), 27.3 (C-3), 16.7 (C-1) and 13.8 ppm (C-4). The C-1 peak has associated tin satellites with a $^1J(^{13}C-^{119}Sn)$ value of 366 Hz. Carbonyl resonances are observed at 184.4, 179.1, 176.5 and 166.3 ppm. From these observations and the general appearance of the $^{13}$C spectrum of the mixture it is apparent that the extract solution contained tributyltins as exemplified in Table 2. However, Fig. 4 does not exactly reproduce Fig. 2 since there are a few notable omissions, e.g. the broad carbonyl feature centred at 172.6 ppm. This is believed to be due to glycerides which are known[12] to be present and extractable from timber and which have had their $^{13}$C spectral

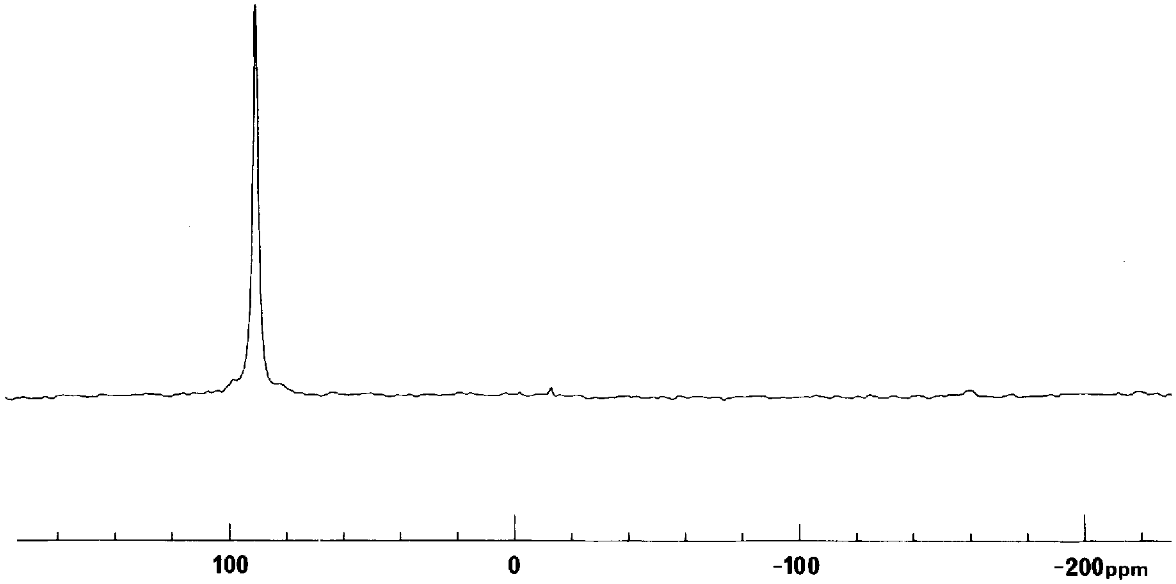


**Figure 3** $^{119}$Sn NMR spectrum of the tributyltin carboxylate solution described in Table 2.

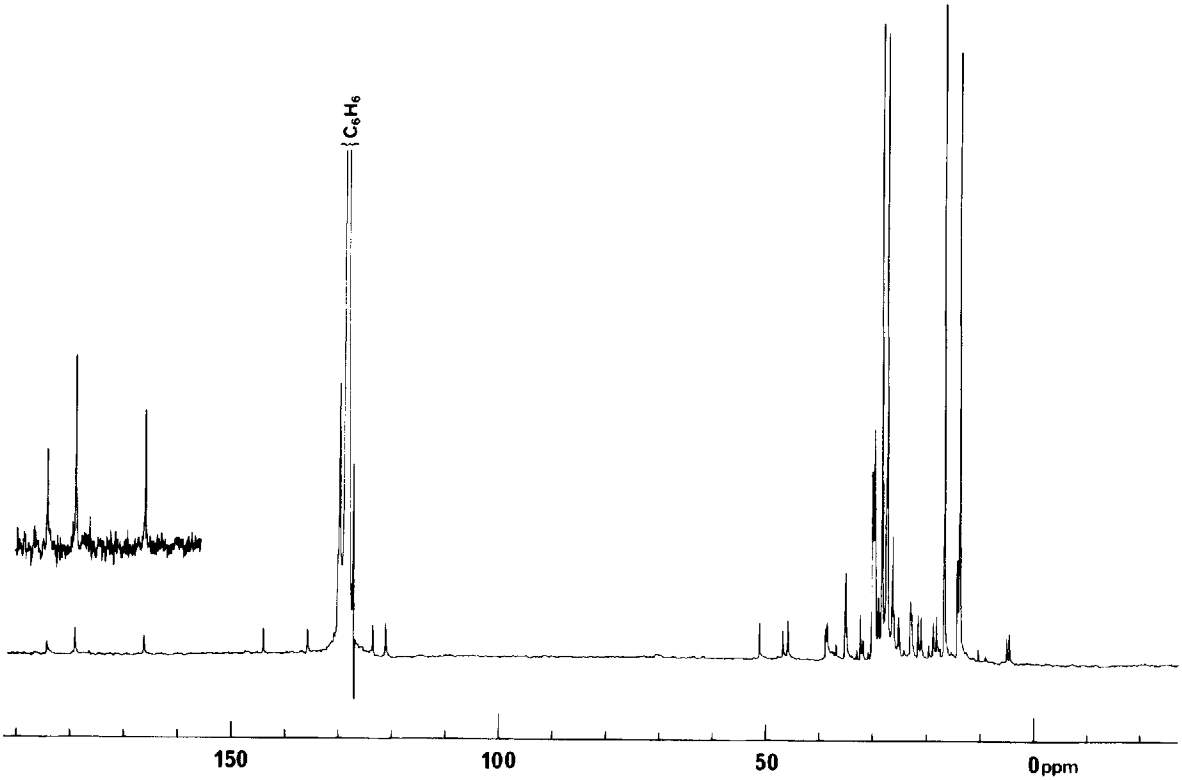


**Figure 4** $^{13}$C NMR spectrum of the tributyltin carboxylate solution described in Table 2.

assignments carried out previously.[15] Associated with the presence of glycerides are a number of small overlapping peaks in Fig. 2 in the region 60–70 ppm due to the —$CH_2$—O moiety of glycerol.

This NMR study has provided evidence for the rapid conversion of $(Bu_3Sn)_2O$ to tributyltin carboxylates in *P. sylvestris* sapwood. Nevertheless, it is possible that this reaction occurred purely on extraction in refluxing benzene. We have, however, demonstrated[5] previously that tributyltin species in *P. sylvestris* sapwood undergo disproportionation to form $Bu_4Sn$ and $Bu_2Sn(OX)_2$ derivatives. If this reaction was occurring on extraction, these species would have been detected in all extracts rather than only in those obtained from the aged (i.e. heated at 60°C for a period of 12 weeks) timber. Thus, the disproportionation reaction must have occurred in the wood. We have additionally shown that both tributyltin linoleate and abietate, as neat liquids, undergo this breakdown process when stored at 60°C, as evidenced by the appearance in their $^{119}Sn$ NMR spectra of peaks at $-155.6$ and $-167.5$ ppm respectively due to $Bu_2Sn(OCO \cdot R)_2$. Bis(tributyltin) oxide, on the other hand, is stable in air at this temperature.[16] Therefore, we believe that the formation of tributyltin carboxylates must be occurring within the timber.

## CONCLUSION

It has been shown that the bulk of $(Bu_3Sn)_2O$ in *P. sylvestris* sapwood undergoes rapid reaction with carboxylic acids, presumably present in the wood resin, to form tributyltin esters, $Bu_3SnOCO \cdot R$. These species can then undergo disproportionation to form $Bu_2Sn(OCO \cdot R)_2$ and $Bu_4Sn$. The latter product is lost to the air by volatilization. In order to prevent this process from occurring it is suggested that alternative tributyltin fungicides, which should not react with carboxylic acids, e.g. $(Bu_3SnO)_3PO$, be used to protect timber.

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