Decomposition of Ethoxyethynyl(trimethyl)tin – Studied by $^{119}$Sn and $^{13}$C NMR Spectroscopy

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The thermally induced decomposition of ethoxyethynyl(trimethyl)tin (1) was studied by $^{119}$Sn NMR which revealed the formation of bis(trimethylstannyl) ketene (2) as the major product, bis(trimethylstannyl) acetic acid ethyl ester (3) as a minor product, and a small amount of tetramethyltin (4). Full NMR data sets, including coupling constants and isotope induced chemical shifts $^{19}$Sn and $^{13}$C ($^{119}$Sn) are provided for 1-3. The first example of ultra-high resolution $^{119}$Sn NMR is shown.

Heating of ethoxyethyne and its derivatives induces thermal decomposition by elimination of ethene to give ketenes [1], followed by various further reactions. Organometallic substituted alkoxynes are attractive starting materials for numerous useful further transformations [2, 3]. Our current interest in the 1,1-organoboration of 1-alkynyltin compounds [4] prompted us to study the decomposition of ethoxyethynyl(trimethyl)tin, Me$_3$Sn-C≡C-OEt (1). 1 reacts readily with triethylborane by 1,1-organoboration [5]; however, prolonged heating at $>$ 80 °C of mixtures containing 1-alkynyltin derivatives and sterically more hindered triorganoboranes is frequently required in order to start the 1,1-organoboration reaction. Therefore, it is important to know how the tin compound behaves under such conditions in the absence of a borane reagent. It has been shown [6a] that 1,1-bis(trimethylstannyl) ketene, (Me$_3$Sn)$_2$C≡C=O (2), can be obtained by heating of 1 to $>$ 80 °C, purified by fractional distillation and characterised by IR, $^1$H and $^{13}$C [6b] NMR spectra. However, coupling constants $^J$(${^{119}}$Sn,${^{13}}$C) and $^{119}$Sn NMR spectra have not been reported. Indeed, $^{119}$Sn NMR should be the ideal tool to reveal the fate of the Me$_3$Sn group in the course of thermal decomposition of 1 in solution.

After heating 1 in [D$_8$]toluene solution at 100 °C for several hours, the reaction mixture becomes dark-coloured, and $^{119}$Sn NMR spectra show that 1 is no longer present. There are mainly three prominent $^{119}$Sn NMR signals amounting to $>$ 98% of the integrated intensities. The major product (ca. 60%) is the ketene 2, followed by bis(trimethylstannyl) acetic acid ethyl ester, (Me$_3$Sn)$_2$CH(O)OEt (3) (ca. 35%), and tetramethyltin, Me$_4$Sn (4) (ca. 4%). In more diluted samples the amount of 3 is noticeably reduced whereas the amount of 4 appears to be slightly increased (Scheme 1). The $^{119}$Sn NMR data were confirmed by $^1$H and $^{13}$C NMR spectra of the same mixtures. The formation of 3 and 4 has not been reported previously. The small amount of Me$_3$Sn is the result of thermally induced redistribution reactions. However, the formation of the ester 3 is somewhat unexpected, since it requires either the reaction of the ketene 2 with ethanol or the intermediary of trimethylstannyl ketene, Me$_3$SnCH=C=O.
Table 1. $^{13}$C and $^{119}$Sn NMR data\(^a\) of the 1-alkynyltin compound 1, bis(trimethylstannyl) ketene 2 and bis(trimethylstannyl) acetic acid ethyl ester 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Me$_3$Sn-C≡C-OEt (1)</th>
<th>(Me$_3$Sn)$_2$C≡C=O (2)</th>
<th>(Me$_3$Sn)$_2$CHC(O)OEt (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{13}$C(Me$_3$Sn)</td>
<td>-7.8 [406.3]</td>
<td>-6.7 [373.9]</td>
<td>-8.0 [345.8]</td>
</tr>
<tr>
<td>$\delta^{13}$C(Sn-C)</td>
<td>33.8 [545.7]</td>
<td>-15.4 [196.1](^b,c)</td>
<td>15.8 [202.3]</td>
</tr>
<tr>
<td>$\delta^{13}$C(CO)</td>
<td>112.1 [130.3]</td>
<td>161.7 [10.5]</td>
<td>176.2 [25.5]</td>
</tr>
<tr>
<td>$\delta^{13}$C(OEt)</td>
<td>74.2 [6.9], 14.2</td>
<td>-</td>
<td>59.5, 14.9</td>
</tr>
<tr>
<td>$\delta^{119}$Sn</td>
<td>-61.5</td>
<td>32.7 [4.8]</td>
<td>23.6 [232.7]</td>
</tr>
<tr>
<td>$\Delta^{12/13}$C($^{119}$Sn)</td>
<td>+1.3 (SnMe$_3$); -51.0 (Sn-C≡); -3.3 (SnMe$_3$); -45.1 (Sn-C=); -11.2 (SnMe$_3$); -8.4 (≡CO)</td>
<td>-4.2 (=CO)</td>
<td>-11.2 (Sn-CH)</td>
</tr>
</tbody>
</table>

\(^a\) In [D$_8$]toluene at 22 ± 1 °C; coupling constants $J(119$Sn,$^{13}$C) and $J(119$Sn,$^{117}$Sn) are given in brackets and curved brackets (± 0.5 Hz), respectively, measured from the $^{13}$C satellites in the $^{119}$Sn NMR spectra using high digital resolution (see Fig. 1). Isotope induced chemical shifts $\Delta$ are given in ppb with a negative sign if the $^{119}$Sn NMR signals of the heavy isotopomer is shifted to lower frequencies;\(^b\) $^2J(=CSn^{13}$C) = 4.6 Hz (see Fig. 2);\(^c\) $^2J(=CSn^{14}$C) = 83.45 Hz. $^1\Delta^{12/13}$C($^{13}$C) ≥ -35.7 ppb (AB pattern of the $^{13}$C satellites was not taken into account).

Fig. 1. 186.5 MHz $^{119}$Sn NMR spectrum of bis(trimethylstannyl) ketene 2 (5% in [D$_8$]toluene, 22 ± 1 °C; 128 transients), recorded by the refocused INEPT pulse sequence [9b,c] (based on $^2J(119$Sn,H$_{Me}$) = 57.6 Hz) with $^1$H decoupling, using a digital resolution of 20 mHz. The line width is ca. 80 mHz. All satellites (as indicated) are clearly resolved.
(not detected in the reaction mixture), which then could react with ethoxy(trimethyl)tin, Me$_3$Sn-OEt (also not detected), to give 3. In any case, this implies that either EtOH or Me$_3$Sn-OEt are formed and trapped in the course of the decomposition of 1.

2 and 3 are attractive examples for applying conditions set up for ultra-high resolution $^{13}$C and $^{119}$Sn NMR spectroscopy. Examples are shown for 2 in Figures 1 and 2. The complete $^{13}$C and $^{119}$Sn NMR data sets of 1, 2 and 3 is given in Table I.

For all three compounds, the coupling constants $J(^{119}$Sn, $^{13}$C) are more readily measured from $^{119}$Sn (Fig. 1) than from $^{13}$C NMR spectra. Furthermore, the $^{119}$Sn NMR spectra reveal the isotope induced chemical shifts $\Delta^{12/13}$C($^{119}$Sn) [8] and confirm the assignments in $^{13}$C NMR spectra. In addition, coupling constants $2J(^{119}$Sn, $^{117}$Sn) are observed in the cases of 2 and 3. The relaxation time of the ketene $^{13}$C nucleus bearing the Me$_3$Sn groups is rather long and therefore, the observation of $^{117/119}$Sn satellites requires much spectrometer time. The application of polarisation transfer [9] from the Me$_3$Sn hydrogen nuclei to this particular $^{13}$C nucleus works very well (Fig. 2): $^{117/119}$Sn satellites are visible already after eight transients, and it proved possible (after 2048 transients) to detect even $^{13}$C satellites corresponding to $1J(^{13}$C=$^{13}$C) = 83.45 Hz for the ketene system. The high resolution achieved in these experiments also allows to observe $^{13}$C satellites due to $2J(^{13}$C$^{13}$C$_{Me}) = 4.6$ Hz.

The sign of $2J(^{119}$Sn, $^{117}$Sn) is negative for coupling across an sp$^3$ hybridised carbon as in 3 or in stannyl-substituted methanes [10]. In 1,1-bis(trimethylstannyl) alkenes $2J(^{119}$Sn, $^{117}$Sn) is large and positive [11]. For 1,1-bis(trimethylstannyl) allenes it was shown that $2J(^{119}$Sn, $^{117}$Sn) is still positive but much smaller than in alkenes [12]. The small value of $2J(^{119}$Sn, $^{117}$Sn) = 4.8 Hz for 2 may be of either sign and shows the strong influence of the nature of the cumulene system on this parameter.

The isotope induced chemical shifts $\Delta^{12/13}$C($^{119}$Sn) follow the pattern which has been established for many organotin compounds [8, 13]. A change in the sign of $\Delta$ is observed for Me$_3$Sn compounds if the magnitude of $1J(^{119}$Sn, $^{13}$C$_{Me})$ exceeds 400 Hz. Although a change of the sign
of \( ^1\Delta^{12/13}C^{(119)Sn} \) are found for different values \(|^1J^{(119)Sn,^{13}C}| \), similar correlations can be expected for any type of carbon atom. It appears that alkynyl \(^{13}C \) nuclei in \(1\)-alkynyl(trimethyl)tin compounds exert the largest negative values of \( ^1\Delta^{12/13}C^{(119)Sn} \).

**Experimental**

The compounds were handled in an atmosphere of Ar and oven-dried glassware was used. The synthesis of ethoxyethynyl(trimethyl)tin 1 followed the literature procedure [6a]. Concentrated (150 mg in 0.5 ml), samples of 1 in \([D_5]\)toluene and diluted (40 mg in 1 ml) samples of 1 under the same conditions were heated to 100 °C up to 12 h. NMR spectra were run on Bruker ARX 250 and DRX 500 spectrometers. Chemical shifts are given relative to MeSi [\(\delta^{(13}C(C_6D_5)=20.4\) ] and MeSn [\(\delta^{119}Sn=0\) for \(\Xi^{(119)Sn}=37.290665\) MHz]. All pulse angles for \(^1H, ^{13}C\) and \(^{119}Sn\) NMR measurements were carefully calibrated, shim parameters were optimised, and low power selective \(^1H\) decoupling was used in order to keep temperature gradients in the sample at a minimum.

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