

Preliminary communication

HYDROSTANNATION OF 1-STANNYL-1-ALKYNES, A REACTION  
 LEADING TO NOVEL VINYL ANION PRECURSORS\*

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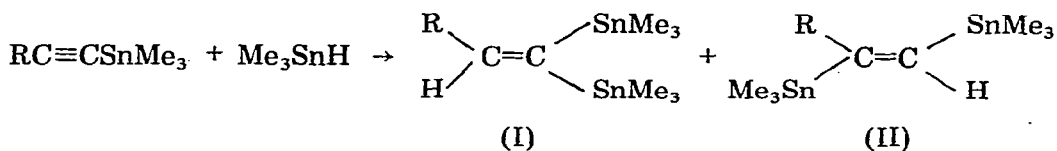
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Summary

Hydrostannation of 1-stannyl-1-alkynes leads to the formation of 1,1-di-stannyl- and 1,3-distannyl-1-alkenes while the reactions of 1-silyl-1-alkynes with a tin hydride are less regiospecific. The 1,1-distannyl-1-alkenes give  $\alpha$ -stannylvinyl anions on treatment with methyllithium

We recently reported [1] the preparation and hydrostannation of stan-nylated allylic alcohols. In the course of that work, we observed that the reaction of trimethyltin hydride with 1-trimethylstannyl-1-hexyne in the presence of azobis(isobutyronitrile) occurs readily and quantitatively, leading almost solely to the bis(trimethylstannyl)-1-hexene of type I (R = n-C<sub>4</sub>H<sub>9</sub>):



To our knowledge, though hydrostannation of terminal and non-terminal acetylenes is well-known [2], the above reaction has not previously been reported. We have since carried out analogous reactions for R = Ph, t-Bu, CH<sub>3</sub>OCH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub> and PhOCH<sub>2</sub> and have also replaced methyl on tin by ethyl: introduction of oxygen into the group R leads to the formation of substantial amounts of 1,3-distannylalkenes of type II, as shown in Table 1. No addition occurs when R = Me<sub>2</sub>Si or Me<sub>3</sub>Sn, even when the reactants are exposed to UV irradiation at low temperature. Except when R = t-Bu, the adducts of type I can undergo a second hydrostannation to give the corresponding tristannylalkanes.

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The adducts of types I and II have been characterised by spectroscopic techniques, including  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR: they are of spectroscopic interest because they provide some of the few values recorded for  $^2J(\text{Sn}-\text{Sn})$  across an  $sp^2$ -hybridised carbon atom and for  $^3J(\text{Sn}-\text{C}=\text{C}-\text{Sn})$  (for other values see refs. 3 and 4). A full report on the NMR spectra of these and related compounds will be published elsewhere [5]; and only tin-tin coupling constants are quoted in Table 1.

TABLE 1

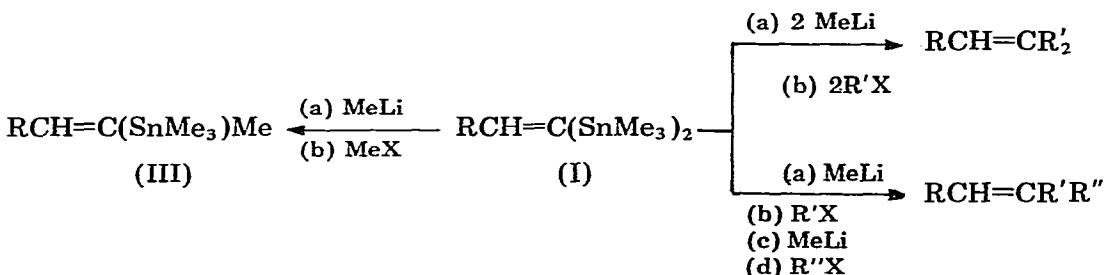
PRODUCTS OF HYDROSTANNATION OF 1-TRIMETHYLSTANNYL-1-ALKYNES  $\text{RC}=\text{CSnMe}_3$ 

R	Ratio I/II <sup>a</sup>	B.p. ( $^{\circ}\text{C}/\text{mmHg}$ ) <sup>b</sup>	$^2J(\text{Sn}-\text{Sn})$ <sup>c</sup>	$^3J(\text{Sn}-\text{Sn})$ <sup>c</sup>
$n\text{-C}_4\text{H}_9$	94/6	$65-68/8 \times 10^{-2}$	693	<i>e</i>
$t\text{-C}_4\text{H}_9$	98/2 <sup>f</sup>	$59/10^{-2}$	684	<i>e</i>
Ph	95/5	$77-86/5 \times 10^{-3}$	580	<i>e</i>
$\text{CH}_3\text{OCH}_2$	63/37 <sup>d</sup>	$60/2 \times 10^{-2}$	603	906
$\text{CH}_2\text{CH}_2\text{OCH}_2$	54/46	$75/3 \times 10^{-2}$	629	941
$\text{PhOCH}_2$	70/30	$102/3 \times 10^{-2}$	540	836

<sup>a</sup> See text. <sup>b</sup> Refers to mixture. <sup>c</sup>  $^nJ(^{119}\text{Sn}-^{119}\text{Sn})$  in Hz. <sup>d</sup> The same ratio was obtained for the bis-(triethylstannyl)alkenes. <sup>e</sup> Not observed. <sup>f</sup> Product obtained by UV-irradiation of reactants: thermal reaction leads to isomerisation of initial product.

The synthetic scope of these adducts lies in the fact that  $\text{Me}_3\text{Sn}$  residues can readily be replaced by lithium [6], for example by treating with methyl-lithium at low temperatures, which provides a route to  $\alpha$ -stannylvinyl carbanions and in principle to vinyl dicarbanions. Proton NMR in fact shows clearly that little or no dicarbanion is formed, only about one equivalent of methyl-lithium being initially consumed; it is important to use methyl-lithium rather than for example butyllithium, because of the existence of alkyl exchange equilibria. Thus treatment of I with 2 equivalents of BuLi leads to the formation of MeLi as the alkyl-lithium in excess, while treatment of  $\text{Me}_4\text{Sn}$  with BuLi under our reaction conditions leads to the formation of  $\text{Me}_3\text{SnBu}$  and MeLi.

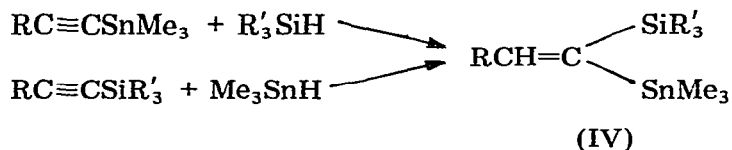
We are at present investigating the synthetic possibilities of adducts I, and have carried out reactions of the following types:



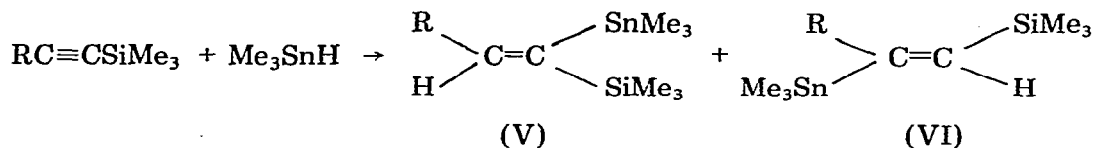
Compound III is formed as an isomer mixture (ratio 1/1) when  $\text{R} = \text{C}_4\text{H}_9$ ; when  $\text{R} = \text{Ph}$ , the (*E*)-isomer is isolated almost exclusively.

Another reagent of potential synthetic use would be a silylstannylalkene of

type IV, which could in principle be obtained by the following two simple routes:



First results indicate that neither route proceeds satisfactorily. Though we have been unable to hydrosilylate silylalkynes with  $\text{Et}_3\text{SiH}$  or  $\text{Cl}_3\text{SiH}$ , the hydrostannation of silylalkynes occurs readily but in a less regiospecific manner than that of stannylalkynes, as shown by the following results:



When  $\text{R} = \text{C}_3\text{H}_7$ , the ratio of compounds V and VI is ca. 1/1, but the product mixture also contains small amounts of the stereoisomers of V and VI.

Replacing propyl by phenyl, however, leads to the expected marked increase in regiospecificity, 90% of the alkene formed being of type V.

Our studies of these hydrostannation reactions and their application in organic synthesis are continuing.

## References

- 1 A. Amamria and T.N. Mitchell, *J. Organometallic Chem.*, 199 (1980) 49.
- 2 B.J. Aylett, *Organometallic Compounds* (4th Ed.), Vol. I, Part 2, pp. 247–249 (Chapman and Hall, 1979)
- 3 B. Wrackmeyer, *Z. Naturforschung (B)*, 33 (1978) 385.
- 4 M. el-Behairy, Dissertation, Dortmund, 1980.
- 5 T.N. Mitchell, in preparation.
- 6 D. Seyferth and L.G. Vaughan, *J. Amer. Chem. Soc.*, 86 (1964) 883.