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The first synthesis of 1,1,2-tristannylalkenes *

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Abstract

The addition of tin–tin bonds to stannyl alkynes to generate 1,1,2-tristannylalkenes occurs readily in the presence of the catalyst system palladium bis(dibenzylideneacetone)/triethyl phosphite.

Introduction

Though tri- [1] and tetrasilylalkenes [2] have been known for some years, the corresponding stannyl derivatives have not so far been described. Distannyl alkenes can be prepared by hydrostannylation of alkynes under free radical conditions [3,4] or by palladium-catalysed addition of ditins to 1-alkynes [5]. The latter reaction is facile for terminal alkynes when $Pd(PPh_3)_4$ is used as the catalyst, but attempts to extend it to include non-terminal alkynes were successful in only a few cases [5,6]. Alkynes of the type $Me_3EC{\equiv}CH$ (E=C, Si, Sn) also resisted all attempts to force them to react.

A recent report [7] that the new catalyst system palladium bis(dibenzylideneacetone)/$P(OCH_2)_3CEt$ induced the addition of hexamethyldisilane to alkynes prompted us to apply this system to the reaction of stannyl alkynes. Our results in this area are reported below.

Results and discussion

The first alkyne used was trimethylstannylethyne, which reacted readily at 70°C with hexamethylditin to give the required tris(trimethylstannyl)ethene, although the reaction did not go to completion even after prolonged reaction times, suggesting that we were dealing with an equilibrium process. Attempts to distil the product led to a large amount of decomposition via the back reaction, thus

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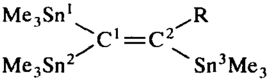
Table 1

Multinuclear NMR data for 1,1,2-tristannylethenes [a]

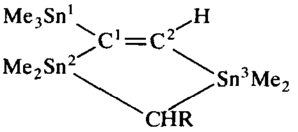
	1	**2**	**4a**	**4b**
$\delta(Sn^1)$	−30.6	−48.0	−30.5	−32.8
$\delta(Sn^2)$	−50.2	−37.7	94.5	87.1
$\delta(Sn^3)$	−81.3	−52.0	56.8	50.1
$^2J(Sn,Sn)$	1011	736	1188 [b]	1078 [b]
$^3J_{cis}(Sn,Sn)$	824	622	736 [c]	936 [c]
$^3J_{trans}(Sn,Sn)$	1513	1070	1546 [d]	1569 [d]
$\delta(C^1)$	176.2	167.6	174.7	175.9
$\delta(C^2)$	167.5	166.4	166.6	167.2
$\delta(C^3)$		194.2 [a]	−19.9	−10.0
$^1J(C_1,Sn)$ [f]	249,366	n.a.	257,320	253, n.o.
$^1J(C_2,Sn^3)$ [f]	467	n.a.	435	418
$^2J(C_1,Sn^3)$ [g]	42	n.a.	28	n.o.
$^2J(C_2Sn)$ [g]	42,66	n.a.	38,56	37,56
$\delta(=CH)$	7.77		8.34	8.30
$^2J(Sn,H)$	132.9		144.4	147.0
$^3J_{cis}(Sn,H)$	174.9		198.8	188.4
$^3J_{trans}(Sn,H)$	268.7		2654.4	253.4

[a] δ In ppm relative to internal Me_4Sn or internal TMS, J in Hz. "Sn" refers to ^{119}Sn. n.a. = not assigned; n.o. = not observed. [b] $^{(2+5)}J$. [c] $^{(3+2)}J$. [d] $^{(3+4)}J$. [e] ester carbonyl. [f] or $^{(1+4)}J$ as appropriate. [g] or $^{(2+3)}J$ as appropriate.

Numbering of atoms as follows:



1, R = H
2, R = CO_2Et



4a, R = H; **4b**, R = Me

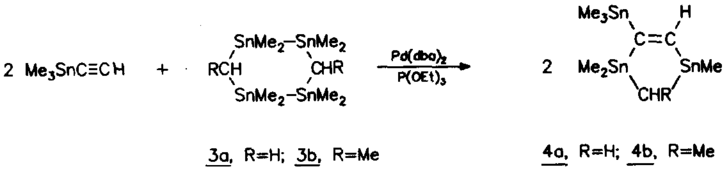
regenerating the starting materials, so that isolated yields were poor. The phosphite ligand used was triethyl phosphite, which we have found to be as effective in promoting palladium-catalysed organotin reactions as is the cyclic phosphite originally suggested [7]. The problem of reversibility was solved by the addition of triphenylphosphine (4 equiv. per equiv. $Pd(dba)_2$) after the reaction had reached the steady state, thus deactivating the catalyst and making possible distillation without decomposition.

We hoped that it would be possible to generalise the reaction to include compounds of the type $Me_3SnC{\equiv}CR$, but of the five substituents so far tried ($R{=}EtO_2C$, Ph, $MeOCH_2$, Me_2NCH_2, Me_3Sn) only the first facilitates the reaction.

$$Me_3SnC{\equiv}CR + Me_3Sn{-}SnMe_3 \xrightarrow{Pd(dba)_2/P(OEt)_3} (Me_3Sn)_2C{=}CR(SnMe_3)$$

$$\mathbf{1}(R = H),\ \mathbf{2}(R = CO_2Et)$$

In the case of compound **2** not even the addition of PPh_3 prevented the back reaction during distillation. Multinuclear NMR spectroscopic examination of the products (Table 1) confirmed their structure, though an exact assignment of the resonances due to the tin moieties was somewhat difficult: we used an increment



model based on the chemical shifts of $Me_3SnCH{=}CH_2$ [8], the three isomeric 1,2-distannylethenes [5,9] and the three isomeric trimethylstannyl derivatives of methyl acrylate [10]. A further attempt to extend the scope of the reaction involved the use of 1,2,4,5-tetrastannacyclohexanes, which we showed several years ago to add to terminal alkynes [11], and we found that the hoped-for reaction did take place (see Scheme 1).

In the case of the reaction of **3b** (R=Me) a side reaction led to the formation of $(Me_3Sn)_2CHMe$ [12] (*ca.* 10%); in the case of **4a**, not only the corresponding product $(Me_3Sn)_2CH_2$ [12] was observed (*ca.* 3%) but also Me_6Sn_2 (*ca.* 10%). Compounds **4** were characterised by multinuclear NMR spectroscopy, and the results of this analysis allowed us to assign the resonances which were previously uncertain; the exocyclic stannyl group can be assigned unambiguously, so the assignment of ^2J(Sn, Sn) and $^3J_{cis}$(Sn, Sn) is also unequivocal. Selective irradiation of the trimethyltin protons to give partially decoupled tin spectra allows the assignment of the coupling constants ^nJ(Sn, H) for the vinylic proton. Work is at present in progress to obtain further corroboration of the signal assignments via a two-dimensional tin–carbon shift correlation [13].

Experimental

All manipulations involving organotin compounds were carried out under argon. NMR spectra were recorded with Bruker AC-200 and AM-300 spectrometers and the mass spectrum with a Finnigan MAT 8230 instrument.

$Pd(dba)_2$ [14] and $Me_3SnC{\equiv}CH$ [15] were prepared by published procedures. $Me_3SnC{\equiv}CCO_2Et$ was obtained from ethyl propiolate, lithium diisopropylamide, and Me_3SnCl as follows: ethyl propiolate (4.9 g, 50 mmol) was added dropwise over 5 min to a solution of LiN^iPr_2 (50 mmol) in 1:1 hexane:THF (70 mL) at −78°C. A solution of Me_3SnCl (10.0 g, 50 mmol) in 5 mL THF was then added dropwise over 20 min. The mixture was allowed to warm to room temperature and stirred overnight. All volatile substances were removed under vacuum and distilled to give the product (b.p. 50°C/0.001 mmHg) as a colourless liquid in 46% yield. Leusink *et al.* [16] had previously described the related preparation of $Et_3SnC{\equiv}CCOOMe$ from methyl propiolate and Et_3SnOMe.

Acyclic tristannylethenes

Equimolar amounts of the trimethylstannylalkyne and hexamethylditin (*ca.* 20 mmol) were heated for 18 h at 70°C in the presence of *ca.* 2 mol% $Pd(dba)_2$ and 4 mol% $P(OEt)_3$. Unconsumed starting materials were removed at 10^{-3} mmHg; after addition of 8 mol% PPh_3 **1** was distilled under vacuum as a light yellow oil:

(44%, b.p. 80°C/0.001 mmHg). Attempts to distil **2** led to considerable decomposition to give the starting materials, the crude yield was *ca.* 75%. Both compounds were characterised by multinuclear NMR spectroscopy (see Table 1), and compound **1** gave a satisfactory elemental analysis (C, H). The mass spectrum (80 eV) of compound **1** showed the molecular ion at m/e 516 (3.9%) and an intense peak (37%) at m/e 353, corresponding to (M^+–$SnMe_3$). The base peak occurred at m/e 165 (Me_3Sn^+).

Cyclic tristannylethenes

A solution of $Me_3SnC{\equiv}CH$ (20 mmol) and the tetrastannacyclohexane **3a** or **3b** (10 mmol) in toluene (30 mL) was heated in the presence of *ca.* 3 mol% $Pd(dba)_2$ and 6 mol% $P(OEt)_3$ for 30 h at 75°C (**3a**) and 15 h at 75°C (**3b**), respectively. Toluene was removed under water-pump vacuum and the products **4a** and **4b** subjected to Kugelrohr distillation at 120°C/0.001 mmHg. This served to separate the organotin compounds from the catalyst, which is stable towards hydrolysis, but not to effect a satisfactory purification of the products. The yields prior to distillation were estimated from the ^{119}Sn NMR spectra to be 80% (**4a**) and 60% (**4b**); after distillation these were reduced to *ca.* 35% and 23% respectively. NMR data for both compounds are given in Table 1.

Acknowledgments

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