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REACTION OF 1,4-PENTADIYNE WITH DIETHYLAMINOTRIMETHYLSTANNANE

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Summary

The reaction between 1,4-pentadiyne and diethylaminotrimethylstannane leads predominantly to (*E*)-2-diethylamino-4-trimethylstannyl-2,4-pentaenyne (with either a 1/1 or 1/2 mol ratio of 1,4-pentadiyne and diethylaminotrimethylstannane). With 1/2 stoicheiometry 1,1,5-tris(trimethylstannyl)penta-1,2-dien-4-yne is formed as a minor product. ^{13}C and ^{119}Sn NMR data are reported.

Introduction

Many alkynylstannanes can be prepared conveniently according to eq. 1. Removal of the dialkylamine, which is readily formed, generally leads to pure compounds [1].

$$n\ R^2C{\equiv}CH + (R^3_2N)_nSnR^1_{3-n} \rightarrow R^1_{3-n}Sn(C{\equiv}CH)_n + n\ R^3_2NH \qquad (1)$$

In previous studies we have shown that alkynylstannanes are interesting precursors of heterocyclic compounds for organoboration reactions [2]. In connection with these studies we attempted the synthesis of 1,4-bis(trimethylstannyl)-1,4-pentadiyne (**4**), with the results described below.

Results and discussion

Since solutions of 1,4-pentadiyne (**1**) in tetrahydrofuran (THF) are readily available [3], a reaction similar to eq. 1 appeared to offer an attractive route. However, the reaction takes a different course, as shown in eq. 2. Compound **3** is obtained in high yield in the 1/1 reaction. With excess of the amide **2** (1/2 reaction) a small amount of the allene derivative **5** was also formed (ca. 8%).

We assume that the formation of compound **3** proceeds via an intermediate **6**, which rapidly rearranges to the allene derivative **7**. The diethylamine which is liberated in the first step probably catalyses this rearrangement and then adds to the allene to give **3** (eq. (3)). This process appears to be stereospecific.

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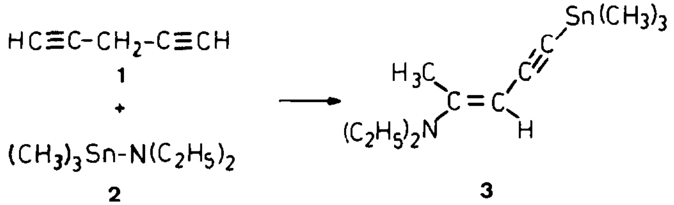
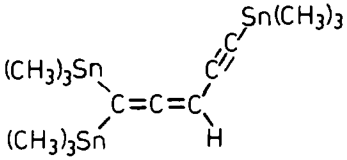


(2)

$(CH_3)_3Sn-C\equiv C-CH_2-C\equiv C-Sn(CH_3)_3$

4



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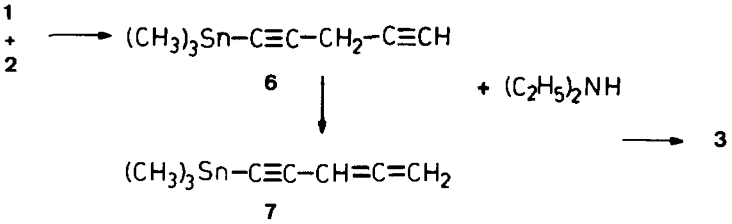

(3)

The ^{13}C and ^{119}Sn NMR data for the compounds **3** and **4** are shown in Table 1. The assignment of the ^{13}C resonances is based upon the magnitude of $^nJ(^{119}Sn-^{13}C)$ [4] and upon the ^1H coupled ^{13}C NMR spectra. The structure of the allene derivative **5** is nicely confirmed by the $\delta(^{119}Sn)$ values [4,5] and by the coupling constants $^nJ(^{119}Sn-^{119}Sn)$ ($n = 2$, 6). The relative position of the substituents at the C=C double bond follows from the $\delta(^{13}C)$ values and from nuclear Overhauser effect (NOE) difference ^1H NMR spectra [6].

It is concluded that reactions of the type shown in eq. 2 offer a convenient way to new enynes.

Experimental

(E)-2-Diethylamino-5-trimethylstannyl-2,4-pentaenyne (3)

Diethylaminotrimethylstannane (**2**) (3.5 g, 15 mM) was added at 20°C under N_2 to a solution of 1,4-pentadiyne (**1**) (16 mM) in 20 ml THF. The mixture was kept for 12 h at 60°C, and its colour changed to orange-red. THF was removed in vacuo and **3** was obtained as a colourless, air-sensitive liquid (3.8 g, 84%, b.p. 86–90°C/10^{-1} Torr) by fractional distillation. Found: C, 48.04; H, 7.73. $C_{12}H_{23}NSn$ calcd.: C, 48.2; H, 7.6%.

When compound **2** was used in excess (7 g, 30 mM), similar work up gave a fraction boiling between 86–96°C/10^{-1} Torr, which was found to contain **3** and ca. 8% (NMR) of compound **5**, and some unidentified impurities in minor amounts (< 3%).

TABLE 1

^{13}C AND ^{119}Sn NMR DATA [a] FOR PRODUCTS 3 AND 5

Compound	$\delta(^{13}C)$ (ppm)						$\delta(^{119}Sn(1))$ (ppm)	$\delta(^{119}Sn(5))$ (ppm)
	C(1)	C(2)	C(3)	C(4)	C(5)	others		
3	16.6	153.4	74.0	111.6	89.3	43.2 (NCH_2)	–	−72.5
						[135.6]		
	–	(5.0)	(14.2)	(110.0)	(506.7)	12.6 (NCH_2CH_3)		
						[126.1]		
						−8.1 ($SnCH_3$)		
	[127.5, 6.8]	–	[157.3, 4.1]	–	–	(402.4)		
						[128.9]		
5								
	79.3	204.2	54.1	105.5	91.6	– [b]($Sn(1)CH_3$)	+1.7	−69.8
$^nJ(^{119}Sn(5)-{}^{13}C)$	–	–	(15.6)	(102.0)	(484.7)	(350.7 [c])	$(105)^2J$	$(52.0)^6J$
$^nJ(^{119}Sn(1)-{}^{13}C)$	(n.o. [d])	(31.2)	(58.0)	(39.7)	(19.1)	– [b] ($Sn(5)CH_3$)		
	–	[3.6]	[170.0]	[4.0]	–	(404.0 [c])		

[a] Bruker WP-200, multinuclear probehead, in 10 mm o.d. tubes, 30% (V/V) solution in $CDCl_3$ at 28°C, $\delta(^{13}C)$ relative to $(CH_3)_4Si$ external, $\delta(^{13}C)$ ($CDCl_3$) 77, $\delta(^{119}Sn)$ relative to $(CH_3)_4Sn$ external, coupling constants $^nJ(^{119}Sn-{}^{13}C)$ and $^nJ(^{119}Sn-{}^{119}Sn)$ in parentheses, coupling constants $^nJ(^{13}C-{}^{1}H)$ in square brackets. [b] Uncertain assignment due to overlap with $^{13}C(Sn-CH_3)$ resonance of **3** and spurious signals. [c] From $^{119}Sn\{^1H\}$-spectra. [d] Insufficient signal/noise ratio.

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