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The palladium-catalysed addition of hexamethylditin to 1,3-dienes

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Abstract

The addition of the tin–tin bond of hexamethylditin to some 1,3-dienes occurs readily in the presence of the catalyst system palladiumbis(dibenzylideneacetone)/triethyl phosphite.

Introduction

We showed several years ago that ditins add readily to 1-alkynes and allenes in the presence of $Pd(PPh_3)_4$ [1]. Attempts to extend this method to include 1,3-dienes met with only very limited success; only in one case did we observe a reaction, and this was unfortunately not reproducible, though the adduct was clearly characterised spectroscopically. A recent report [2] that the new catalyst system palladiumbis(dibenzylideneacetone)/$P(OCH_2)_3CEt$ induced the previously unknown addition of hexamethyldisilane to alkynes prompted us to apply this more reactive system to the ditin/diene reaction. Other workers have examined the related addition of silylstannanes to 1,3-dienes and found it necessary to use a platinum catalyst to effect the reaction [3]. In the light of this report we felt it timely to describe the results of our investigations.

Results and discussion

In the course of our work on the addition of ditins to unsaturated systems, we attempted to add hexamethylditin to 1,3-dienes using $Pd(PPh_3)_4$ as catalyst and in the case of isoprene obtained the expected adduct as a single isomer in 17% yield:

$$H_2C{=}C(Me)CH{=}CH_2 + Me_6Sn_2 \xrightarrow{Pd(PPh_3)_4} \underset{\textbf{1b}}{Me_3SnCH_2C(Me){=}CHCH_2SnMe_3}$$

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Sakurai *et al.* had reported [4] that the analogous reaction of hexamethyldisilane afforded a 1:2 adduct with *E* geometry, while 1,1,2,2-tetramethyldisilane reacted with isoprene under the influence of a nickel catalyst to give a 1:1 adduct with *Z* stereochemistry [5]. It has been reported very recently that 1,1,2,2-tetramethyl-1,2-dichlorogermane reacts with isoprene under palladium catalysis to give a 1:1 *E*-adduct [6]. In order to determine the stereochemistry of our product, we synthesised a mixture of *Z*- and *E*-1,4-bis(trimethylstannyl)-2-butene **1a** in two different ways: (i) from 1,4-dibromo-2-butene and Me_3SnLi in tetrahydrofuran (THF) and (ii) from magnesiumbutadiene [7] and Me_3SnBr.

$$\begin{tikzcd} E/Z\text{—}BrCH_2CH{=}CHCH_2Br + 2Me_3SnLi \arrow[dr] & \\ & E/Z\text{—}Me_3SnCH_2CH{=}CHCH_2SnMe_3 \\ \text{-}\!(Mg\text{—}CH_2CH{=}CHCH_2\text{-}\!)_n + 2Me_3SnBr \arrow[ur] & \end{tikzcd}$$

In the former case, as expected, a 1:1 isomer mixture was obtained, while in the latter the ratio was 4:1. Chemical arguments [7] indicated the major isomer in the latter case to be the *Z* isomer, and we initially assigned the isomers on this basis. ^5J(Sn,Sn) was 370 Hz for the minor (*E*) and 306 Hz for the major (*Z*) isomer, while the product from the ditin/isoprene addition exhibited a coupling of 279 Hz, thus indicating it to have *Z* geometry.

Since the ditin/isoprene addition was not readily reproducible and apparently not extendable to other 1,3-dienes, a break in our investigations of several years followed. We returned to this chemistry in the course of our studies into the efficacy of a new catalyst precursor system, $Pd(dibenzylideneacetone)_2/P(OEt)_3$, derived by replacing the phosphite ligand originally used by Tanaka et al. [2] by triethyl phosphite. This more efficient catalyst system did indeed prove to be suitable for inducing a reaction between butadiene, isoprene, or 2-phenylbutadiene and hexamethylditin, though the reaction was apparently reversible, prolonged reaction times not increasing the yields above a certain point. In addition, an attempt to distil the adduct derived from isoprene led to complete decomposition to regenerate the starting materials. In the light of earlier experience, we attempted to deactivate the catalyst when the steady state had been reached by adding Ph_3P (4 equiv. per equiv. $Pd(dba)_2$) or $Ph_2PCH_2CH_2PPh_2$ (2 equiv. per equiv. $Pd(dba)_2$); this procedure permitted distillation of all three adducts without decomposition.

In all cases a single isomer was obtained, that derived from isoprene being identical to the product obtained earlier. The product from butadiene had a value for ^5J(Sn,Sn) of 306 Hz, thus suggesting it to be *Z*-**1a**, while the value for the 2-phenylbutadiene adduct **1c** (275 Hz) indicated that it also had the same geometry as the other two products. At this point our conclusion was thus that the palladium-catalysed addition of hexamethylditin to 1,3-dienes occurs in a stereospecific manner to give products of *cis*-addition; however, no final spectroscopic proof was available at this point. A number of other derivatives of 1,3-butadiene (1-phenylbutadiene, 1,4-diphenylbutadiene, 2,3-dimethylbutadiene, 1-methyl-2-phenylbutadiene, 2-trimethylsiloxybutadiene) were tested and found to be unreactive when treated with hexamethylditin.

Table 1

NMR data for compounds of the type Z/E-$Me_3Sn^1C^1H_2C^2R{=}C^3HC^4H_2Sn^2Me_3$

	Z-**1a**	*E*-**1a**	*Z*-**1b** [a]	*Z*-**1c** [b]
$\delta(Sn^{1/2})$	−3.3	−4.9	−1.6/−3.2	−0.6/−0.7
$^5J(Sn,Sn)$	306	370	279	275
$\delta(\mathit{C}H_3Sn)$	−10.3	−9.8	−9.1/−9.6	−9.0/−9.3
$^1J(C,Sn)$	319	319	310/313	317/317
$\delta(C^{1/4})$	12.0	15.9	17.5/13.0	15.0/15.2
$^1J(C,Sn)$	310	326	303/316	295/303
$\delta(C^{2/3})$	122.7	124.2	117.5/129.8	121.7/134.0
$^2J(C,Sn)$	50.6	51.4	52/53	56/50
$\delta(C\mathit{H}_3Sn)$	0.08	0.04	0.08/0.11	0.03/0.22
$\delta(C\mathit{H}_2)$	1.64	1.65	1.57/1.64	1.89/2.16
$^3J(H,H)$	10.0	n.d.	8.9	9.1
$\delta({=}C\mathit{H})$	5.28	5.26	5.05	5.83
$^3J(H,H)$	9.8	15.3		

δ in ppm w.r.t. Me_4Sn or TMS, J in Hz. n.d.: not determined. [a] methyl group: δ(C) 25.6, δ(H) 1.66. [b] phenyl group: δ(C) 125.5, 125.7, 128.5, 144.3.

The determination of the value of $^3J(H,H)$ in the vinyl fragment of *Z*- or *E*-**1a** is unfortunately not a trivial matter because of chemical equivalence and also overlap of the sets of signals from the two isomers, even at 300 MHz. Since this coupling constant provides the unequivocal proof required, we used the techniques devised by Radeglia [8] to determine its magnitude (details of these experiments will be published elsewhere [9]). Within experimental error, the values obtained are 9.8 Hz for the compound which we had originally (correctly) assumed to be the *Z* isomer and 15.3 Hz for the second (*E*) isomer.

Multinuclear NMR data were obtained for compounds **1a**–**1c** and are collected in Table 1. Though some data for *Z*- and *E*-**1a** have been reported previously [10] these are included here for comparison. Assignment of the resonances in *Z*-**1b** and *Z*-**1c** was carried out using two-dimensional tin–carbon NMR correlation spectroscopy [11]; details of these experiments will be given elsewhere [9].

Experimental

All manipulations involving organotin compounds were carried out under argon. NMR spectra were recorded with Bruker AC-200 and AM-300 NMR spectrometers.

Reaction of isoprene with Me_6Sn_2

(i) using $Pd(dba)_2/P(OEt)_3$ *as catalyst.* A mixture containing Me_6Sn_2 (32.4 g, 99 mmol), isoprene (20.4 g, 300 mmol), $Pd(dba)_2$ (1.13 g, 2 mol%) and $P(OEt)_3$ (0.65 g, 4 mol%) was heated for 6 h at 60°C. Excess isoprene was removed at the water pump and the unchanged ditin pumped off at room temperature under a pressure of 0.01 mmHg. The residue was treated with PPh_3 (2.1 g, 8 mol%) and distilled. *Z*-2-Methyl-1,4-bis(trimethylstannyl)-2-butene **1b** (22.6 g, 58%) was obtained as a colourless oil, b.p. 60°C/0.001 mmHg.

(ii) using $Pd(PPh_3)_4$ *as catalyst.* A mixture containing Me_6Sn_2 (5.0 g, 15.3 mmol), isoprene (1.04 g, 15.3 mmol) and $Pd(PPh_3)_4$ (2 mol%) was heated for 15 h

at 85°C. NMR spectroscopy indicated 30% consumption of the ditin. Excess isoprene was removed at the water pump, unreacted ditin using a vacuum pump. The residue was distilled, giving Z-**1b** (1.0 g, 17%) as a colourless oil. Anal. Found: C, 33.30; H, 6.90. $C_{11}H_{26}Sn$ calc.: C, 33.29; H, 6.62%.

Reactions of 2-phenylbutadiene and butadiene with Me_6Sn_2

The reaction of 2-phenylbutadiene to give Z-**1c** was carried out on a 60-mmol scale using equimolar amounts of the ditin and the diene (reaction conditions: 24 h/70°C). Different reaction conditions were necessary for the reaction of butadiene to give Z-**1a**; butadiene gas (99% purity) was passed through a column packed with molecular sieve into the reaction flask containing the ditin (6.5 g, 20 mmol) and the catalyst $Pd(dba)_2/P(OEt)_3$ (2/4 mol%): The reaction was carried out at 60°C for 6 h. In each case the catalyst was deactivated with Ph_3P prior to distillation. Isolated yields and boiling points were as follows: Z-**1a** (16%), b.p. 45°C/0.001 mmHg; Z-**1c** (43%), b.p. 120°C/0.001 mmHg.

Reaction of 1,4-dibromo-2-butene with Me_3SnLi

A solution of 1,4-dibromo-2-butene (5.0 g, 23.4 mmol, Z/E mixture) in THF (40 mL) was added dropwise to a 0.77 *M* solution of Me_3SnLi (in THF (61 mL, 47 mmol) at −78°C. When the addition was complete the mixture was stirred for 1 h, allowed to warm to room temperature, and subjected to the usual aqueous work-up. THF was distilled off and the residue fractionated *in vacuo*. The main product was Me_6Sn_2, but **1a** (1.4 g, 16%) was isolated as a 1:1 mixture of Z and E isomers. Anal. Found: C, 31.90; H, 6.60. $C_{10}H_{24}Sn_2$ calc.: C, 31.47; H, 6.34%.

Reaction of magnesium butadiene [7] with Me_3SnBr

Magnesium butadiene (2.3 g, 10.3 mmol) was suspended in THF (30 mL); a solution of Me_3SnCl (3.9 g, 19.7 mmol) in THF (30 mL) was added dropwise, giving a clear solution, which was heated for 1 h under reflux. The usual aqueous work-up followed. THF was distilled off and the residue fractionated to give **1a** (1.4 g, 36%) was obtained as a 4:1 mixture of Z and E isomers.

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