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A facile stereoselective synthesis of 1,3-dienyl sulfones via Stille coupling reactions of (*E*)-α-stannylvinyl sulfones with alkenyl iodides

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Abstract

Palladium-catalyzed hydrostannylation of acetylenic sulfones **1** in benzene at room temperature gives stereoselectively (*E*)-α-stannylvinyl sulfones **2** in good yields. (*E*)-α-Stannylvinyl sulfones **2** are new difunctional group reagents which undergo Stille coupling reactions with alkenyl iodides **3** to afford stereoselectively 1,3-dienyl sulfones **4** in high yields.

Keywords: Hydrostannylation; Acetylenic sulfone; (*E*)-α-Stannylvinyl sulfone; Stille coupling; 1,3-Dienyl sulfone; Stereoselective synthesis

1. Introduction

The stereocontrolled synthesis of conjugated dienes attracts considerable interest in organic chemistry because of their appearance in a wide variety of biologically active molecules and their key synthetic intermediates [1]. The synthesis of 1,3-dienes for use in the Diels–Alder reaction is still an important challenge in organic synthesis [2] although other elegant uses of these compounds have been developed [3]. Conjugated dienes are usually prepared by utilizing either a Wittig-type approach [4] or the transition metal-catalyzed coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds [5]. Recently, Whitby and co-workers [6] reported the insertion of 1-lithio-1-halobutadiene into organozirconocenes providing a stereocontrolled synthesis of (*E*,*Z*)-1,3-dienes.

The stereocontrolled synthesis of 1,3-dienes containing metal or heteroatom functional groups is also of considerable interest in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions [7]. Heteroatom-substituted 1,3-dienes are also useful precursors to construct highly functionalized ring systems in Diels–Alder reactions [8]. The stereoselective synthesis of 1,3-dienylsilanes [9], 1,3-dienyl sulfides [10], 1,3-dienyl selenides [11], and 1,3-dienylstannanes [12] has already been described in the literatures. 1,3-Dienyl sulfones are extensively used as intermediates in organic synthesis [13] due to the chemical versatility of the sulfone moiety. 1,3-Dienyl sulfones are also excellent acceptors in Michael additions [14] and 2π partners in cycloaddition reactions [15]. However, the stereocontrolled synthesis of 1,3-dienyl sulfones has rarely aroused extensive attention [16]. The Stille coupling reactions of vinylstannanes with alkenyl iodides provides a convenient route to stereoselective synthesis of 1,3-dienes [17]. Allred and Liebeskind [18] reported that α-(tributylstannyl)thiophene and alkenyl iodides were successfully Stille-coupled to afford different products containing sulfur-substituted 1,3-diene structural skeleton. Herein, we wish to report that 1,3-dienyl sulfones could be conveniently synthesized by the palladium-catalyzed hydrostannylation of acetylenic sulfones, followed by a Stille coupling reaction with alkenyl iodides.

2. Results and discussion

Palladium-catalyzed hydrostannylation of alkynes provides a simple general route for the synthesis of vinylstannanes [19]. Palladium-catalyzed hydrostannylation of

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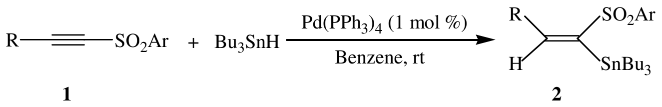
thioacetylenic compounds [20], alkynyl selenides [21], and alkynyl sulfoxides [22] has been reported to be highly regio- and stereoselective, providing a direct route for the stereoselective synthesis of 1,1-difunctional group reagents containing heteroatom and tin. Recently, the palladium-catalyzed hydrostannylation of propargylic sulfones has also been described [23]. However, to the best of our knowledge, no palladium-catalyzed hydrostannylation of acetylenic sulfones has been described so far. We investigated the palladium-catalyzed hydrostannylation of acetylenic sulfones in order to prepare (*E*)-α-stannylvinyl sulfones. Our initial efforts were devoted to the selection of an efficient catalyst and a suitable solvent for highly regio- and stereoselective hydrostannylation reaction of acetylenic sulfones **1** with Bu_3SnH. Thus, 1-butyl-2-(phenylsulfonyl)ethyne **1a** (1 mmol) and Bu_3SnH (1.05 mmol) were treated in THF or benzene (4 ml), at room temperature, with Pd(0) and Pd(II) catalysts (Table 1). As shown in Table 1, among the palladium catalysts tested [$Pd(OAc)_2$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, and $PdCl_2$], $Pd(PPh_3)_4$ proved to be the most efficient. Both THF and benzene could be used as the solvent, the use of benzene was the best choice. Increasing the amount of $Pd(PPh_3)_4$ could shorten the reaction time, but did not increase the yield of (*E*)-1-(tributylstannyl)-1-(phenylsulfonyl)-1-hexene (**2a**). Taken together, excellent result was obtained when the hydrostannylation reaction was carried out with 1 mol% $Pd(PPh_3)_4$ in benzene at room temperature for 4 h under an argon atmosphere.

To examine the scope for this hydrostannylation reaction, the hydrostannylation reactions of a variety of acetylenic sulfones **1** with Bu_3SnH were investigated under the optimum conditions (Scheme 1), the experimental results are summarized in Table 2. As shown in Table 2, the palladium-catalyzed hydrostannylation reactions of a variety of acetylenic sulfones **1** with Bu_3SnH proceeded smoothly at room temperature in benzene giving the corresponding (*E*)-α-stannylvinyl sulfones **2** in good to high yields. Investigations of the crude products **2** by ^1H NMR spectroscopy (400 MHz) showed their isomeric purities of more than 98%. One olefinic proton signal of compounds **2a**, **2b**, **2d**, and **2e** splits characteristically into one triplet at $\delta = 6.25–6.42$ with coupling constant $J = 4.8–7.2$ Hz, which indicated that the hydrostannylation to the acetylenic sulfones had taken place with strong preference for the addition of the tin atom at the carbon adjacent to the sulfonyl group. The stereochemistry of the addition was readily apparent from the ^1H NMR spectra of compounds **2** which showed a ($^3J_{Sn117–H}$) coupling constant of 48–52 Hz, fully in accord with an *E* geometry and overall cis addition of tin hydride [24].

Table 1
Catalytic activity of several palladium complexes and effect of solvents[a]

Entry	Catalyst (mol%)	Solvent	Time (h)	Isolated yield **2a** (%)
1	$Pd(OAc)_2$ (1)	THF	24	0
2	$Pd(OAc)_2$ (1)	Benzene	24	0
3	$PdCl_2(PPh_3)_2$ (1)	THF	6	51
4	$PdCl_2(PPh_3)_2$ (1)	Benzene	6	63
5	$Pd(PPh_3)_4$ (1)	THF	4	71
6	$Pd(PPh_3)_4$ (1)	Benzene	4	90
7	$Pd(PPh_3)_4$ (5)	Benzene	2	89
8	$PdCl_2$ (1)	THF	24	0
9	$PdCl_2$(1)	Benzene	24	0

[a] Reactions were performed with **1a** (1 mmol), Bu_3SnH (1.05 mmol), solvent (4 ml) at room temperature under Ar.



Scheme 1.

Table 2
Synthesis of (*E*)-α-stannylvinyl sulfones **2a–e**[a]

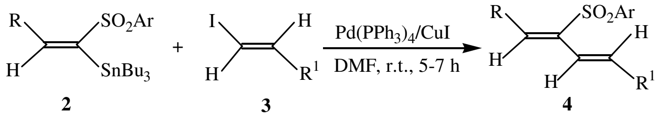
Entry	R	Ar	Product	Yield[b](%)
1	*n*-C_4H_9	Ph	**2a**	90
2	*n*-C_4H_9	4-$CH_3C_6H_4$	**2b**	88
3	Ph	Ph	**2c**	82
4	CH_3OCH_2	Ph	**2d**	83
5	CH_3OCH_2	4-$CH_3C_6H_4$	**2e**	80

[a] Reactions were performed in the presence of **1** (1 mmol), Bu_3SnH (1.05 mmol), $Pd(PPh_3)_4$ (0.01 mmol), using benzene (4 ml) as solvent, at room temperature for 4 h under Ar.

[b] Isolated yield based on the **1** used.

(*E*)-α-Stannylvinyl sulfones **2** are new difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl sulfones. With a convenient route to the (*E*)-α-stannylvinyl sulfones **2**, we decided to establish the feasibility of using **2** in Stille coupling reactions with alkenyl iodides **3**. We observed that, when the coupling reactions of **2** with a variety of alkenyl iodides **3** were performed in DMF at room temperature using $Pd(PPh_3)_4$ and CuI as co-catalyst (Scheme 2), fairly rapid reactions occurred affording stereoselectively the desired coupling products **4** in high yields. The experimental results are summarized in Table 3. The coupling reaction of **2** with alkenyl bromides was very slow under the same reaction conditions, only traces of coupling products were obtained after 24 h of reaction time. The coupling reaction of **2** with alkenyl chlorides did not occur at all.

It is well documented that the cross-coupling reaction (Stille coupling) of vinylstannanes with organic halides in the presence of a palladium catalyst occurs with retention of configuration [25]. The *E*-configuration of the compounds **4a–i**, and **4l–n** has been proved by their ^1H NMR



Scheme 2.