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Reactivity of *tert*-butanesulfinamides in palladium-catalyzed allylic substitutions

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ABSTRACT

The performance of *tert*-butanesulfinamides as nitrogen nucleophiles in Pd(0)-catalyzed allylic substitution reactions has been investigated. Metalated *N*-alkyl and *N*-acetyl sulfinamides have been identified as suitable partners for the reaction with π-allyl–palladium complexes. The cross-coupling of *N*-acetyl *tert*-butanesulfinamide with 2- or 3-substituted linear allylic carbonates is achieved in the presence of $Pd(OAc)_2$ (5 mol%) and dppe (7.5 mol%) and does not require an additional base. The reaction proceeds in high yields (59–98%) to produce the corresponding *E*-configured linear allylic sulfinamides in a totally regioselective and highly diastereoselective manner. The sulfur atom remains configurationally stable throughout the allylation process, and thus the coupling products are obtained in enantiomerically pure form.

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1. Introduction

The use of the chiral amine reagent *tert*-butanesulfinamide **1a** (Scheme 1) has attracted a great deal of attention over the last decade and has found applications in an increasingly growing number of research fields [1]. In the context of asymmetric synthesis, it is now a well-established tool for the preparation of chiral non-racemic amines. Rapid access to both enantiomeric forms of *tert*-butanesulfinamide, high levels of stereodiscrimination and easy removal of the sulfinyl moiety under mild acidic conditions constitute major advantages to the use of the *N*-*tert*-butanesulfinyl group as chiral auxiliary. Furthermore, *tert*-butanesulfinamides have also found promising applications in the field of asymmetric catalysis, where they have been successfully used as ligands for transition metal catalysts or organocatalysts [1].

An impressive body of work has been devoted to the preparation of elaborated enantiopure *tert*-butanesulfinamides and the area has been recently reviewed extensively [1,2]. The vast majority of synthetic approaches entails the condensation of **1a** with a carbonyl derivative and the subsequent reaction at the electrophilic carbon atom of the corresponding sulfinimine thereby produced [2]. Quite surprisingly, the complementary synthetic strategies utilizing *tert*-butanesulfinamides as chiral nitrogen nucleophiles have received far less attention [3]. Furthermore, their use as partners in metal-catalyzed amination reactions is an interesting prospect that has only been successfully exploited very recently. Arylation of *tert*-butanesulfinamide with aryl- and heteroaryl halides has been reported using Cu [4] and Pd [5] catalysts. *tert*-Butanesulfinamides have also been shown to be efficient partners for the Pd-catalyzed Wacker-type aerobic oxidative cyclization of tethered alkenes [6]. Finally, the Pd-catalyzed [3 + 2] cycloaddition of *N*-*tert*-butanesulfinimines with trimethylenemethane is as well a related process that involves a carbon–nitrogen bond formation [7].

In this context, and given the recent interest in allylic *N*-*tert*-butanesulfinamides as hybrid ligands for asymmetric catalysis [8], we have considered the use of *tert*-butanesulfinamides as nitrogen

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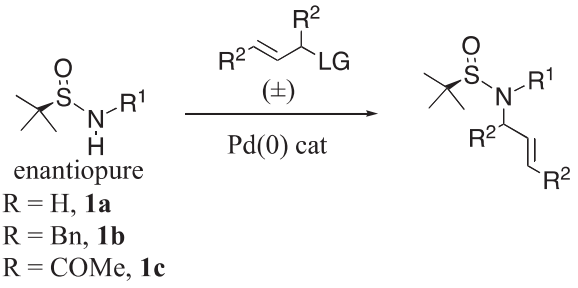


Scheme 1. Proposed strategy to prepare enantiopure allylic sulfinamides.

nucleophiles in Pd(0)-catalyzed allylic substitution reactions [9] (Scheme 1). To the best of our knowledge, the only precedent for such a transformation is that of Pyne and co-workers. These authors reported that lithiated **1a** reacts with cyclohex-2-enyl ethyl carbonate in the presence of 5 mol% [$Pd(PPh_3)_4$] to afford the corresponding sulfinamide, albeit in poor yield and diastereoselectivity [10]. Furthermore, the substitution product was described to undergo rapid hydrolysis in the presence of silica-gel. Intrigued by this reported unstability, we decided to reinvestigate this reaction using other nitrogen-substituted sulfinamides and acyclic electrophiles. Hereafter, we disclose our first findings concerning this approach.

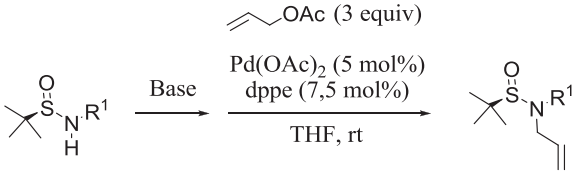
2. Results and discussion

2.1. Allylic substitution with allyl acetate

Initially, we decided to identify nucleophiles derived from *tert*-butanesulfinamide that would be well-suited to react with standard π-allyl–palladium complexes. Towards this end, we selected as archetypal reaction the allylic substitution of allyl acetate (3 equiv), using as catalytic system a combination of $Pd(OAc)_2$ (5 mol%) and dppe [1,2-bis(diphenylphosphino)ethane] (7.5 mol%) in THF (Table 1). In the presence of K_2CO_3, allylation of sulfinamides **1a** or **1b** was at most very sluggish (entries 1 and 3), thereby indicating that *N*-alkyl *tert*-butanesulfinamides are not nucleophilic enough to intercept the π-allyl complex intermediate in these conditions. By contrast, their corresponding lithium salts, obtained by treatment with 1 equiv ^{n}BuLi, took part readily in the nucleophilic substitution. For unsubstituted sulfinamide **1a**, the expected product **2a** was only obtained in 8% yield as the process was hampered by the competitive acylation reaction of the lithium salt of **1a** with the ester moiety of allyl acetate (entry 2). However, in the case of substituted sulfinamide **1b**, the allylated compound **2b** was isolated in 83% yield (entry 4). Finally, starting from acetyl-substituted pronucleophile **1c**, the allylation product **2c** was obtained in good 70–95% yields either by reacting the pre-formed lithium or sodium salts of **1c** (entries 5 and 6), or in the presence of K_2CO_3 (entry 7). For these last reaction conditions, it is likely that the carbonate base is strong enough to deprotonate **1c** (quantitatively or at least to a great extent), thereby generating *in situ* the reactive nucleophile.

Worthy of mention, the unforeseen acylation of the lithium salt of **1a** in the presence of allyl acetate led us to consider a one-pot strategy leading to the sequential acylation/allylation of *tert*-butanesulfinamide **1a** (Scheme 2). Treatment of **1a** with ^{n}BuLi, followed by the addition of methyl acetate led to the formation of the lithium salt **3** that was then engaged directly in the palladium(0)-catalyzed allylation. Product **2c** was obtained in excellent 95% yield using only a slight excess of allyl acetate.

Table 1
Pd(0)-catalyzed allylic substitution of allyl acetate by metalated sulfinamides.



Entry	Substrate	R^1	Base	Product	Yield[a]
1	**1a**	H	K_2CO_3[b]	**2a**	11%
2	**1a**	H	^{n}BuLi[c]	**2a**	8%[d]
3	**1b**	Bn	K_2CO_3[b]	**2b**	No reaction
4	**1b**	Bn	^{n}BuLi[c]	**2b**	83%
5	**1c**	COMe	^{n}BuLi[c]	**2c**	83%
6	**1c**	COMe	NaH[e]	**2c**	95%
7	**1c**	COMe	K_2CO_3[b]	**2c**	70%

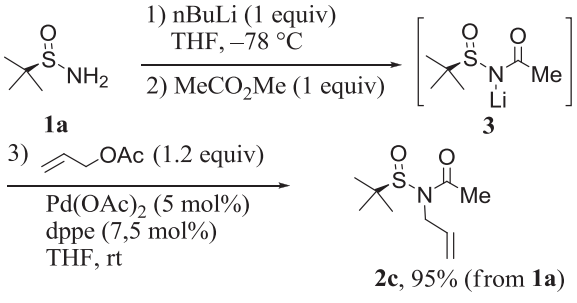
[a] Yield of isolated product after column chromatography.
[b] K_2CO_3 (3 equiv) was added to the reaction medium.
[c] Deprotonation conditions: ^{n}BuLi (1 equiv), THF, −30 °C, 0.5 h.
[d] 85% of acetylated product **2c** was also isolated.
[e] Deprotonation conditions: NaH (1 equiv), THF, 0 °C, 0.5 h.

Having identified metalated sulfinamides as competent nucleophiles for allylic substitution, we considered to use the BSA [*N*,*O*-bis(trimethyl)acetamide]/AcOK system [11] as an alternative to the discrete pre-formation of the metalated nucleophiles (Table 2). Pleasingly, sulfinamide **1a** underwent allylation with allyl acetate in refluxing THF using the $Pd(OAc)_2$/dppe catalytic system in the presence of BSA (1.1 equiv) and AcOK (10 mol%). *N*-Allyl *tert*-butanesulfinamide **2a** was isolated in 56% yield, despite the formation of 16% of *N*,*N*-diallyl *tert*-butanesulfinamide (entry 1). While no reaction was observed with benzyl-substituted sulfinamide **1b** (entry 2), efficient allylic substitution was restored in the case of the acetyl-substituted sulfinamide **1c** (entry 3).

These results suggest that the *in situ* generated *N*-(trimethylsilyl)acetamide is basic enough to deprotonate unsubstituted *tert*-butanesulfinamide **1a** and *N*-acyl-substituted **1c**, thereby efficiently generating a nucleophile suitable for the substitution to occur. Conversely, this silylated base does not metalate *N*-benzyl *tert*-butanesulfinamide **1b**.

2.2. Allylic substitution with allylic carbonates

We considered next to use allylic carbonates as electrophilic partners. Given that *N*-acetyl *tert*-butanesulfinamide **1c** undergoes allylation in the presence of K_2CO_3, we reasoned that in this case an additional base might be avoided as the carbonate leaving group could be basic enough to deprotonate the starting material and thus generate the nucleophile for the coupling reaction (Scheme 3).



Scheme 2. One-pot acylation/allylation of *tert*-butanesulfinamide **1a**.

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