



Addition of a carbamoylsilane to *N*-sulfonylimines: direct synthesis of α -(*N*-sulfonyl)amino-*N*-methoxymethyl-*N*-methylamides



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ABSTRACT

N-Methoxymethyl-*N*-methylcarbamoyl(trimethyl)silane reacted with *N*-sulfonylimines in anhydrous benzene under catalyst-free conditions to afford α -(*N*-sulfonyl)amino-*N*-methoxymethyl-*N*-methylamides in good to excellent yields (71–95%). Furthermore, after acid hydrolysis at room temperature, the corresponding α -(*N*-sulfonyl)amino secondary amides can be formed.

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Introduction

α -Aminoamides are representatives of the smallest subunit of peptides and proteins, and found in a wide range of natural products and pharmaceuticals.¹ They have also been used as intermediates for the synthesis of different heterocycles.² Due to such interests, numerous methods for the synthesis of α -aminoamides have been developed. Among them, the Ugi reaction has been intensively studied over the past decades,³ in which a multicomponent mixture of primary amine, carboxylic acid, aldehyde, and isocyanide affords an α -(*N*-acyl-*N*-alkyl amino)amide, whose various limitations are under continual improvement.⁴ Recently, Mita et al. reported that the catalytic silylation of *N*-benzenesulfonylimines using a Cu-secondary diamine complex as catalyst, then carboxylation under a CO₂ atmosphere can afford α -aminoacids.⁵ We have also used sulfonylimines as the reaction substrates to react with *N,N*-dimethylcarbamoyl(trimethyl)silane under catalyst-free conditions, successfully realized the formation of the α -(*N*-sulfonyl)aminoamides in a single step.⁶ However, these results specifically address the formation of (tertiary) *N,N*-dimethylamides, for efficient application within these areas, the synthesis of α -amino secondary amides is required. To the best of our knowledge, carbamoylsilane has never been reported for the synthesis of α -amino secondary amides. We have tested this process using *N*-methoxymethyl-*N*-methylcarbamoyl(trimethyl)

silane as a secondary amide source and reported here our results about the synthesis of α -(*N*-sulfonyl)amino-*N*-methoxymethyl-*N*-methyl amides (Scheme 1). *N*-Methoxymethyl group of α -(*N*-sulfonyl)amino-*N*-methoxymethyl-*N*-methyl amides **3** could be easily converted into hydrogen atom by acid hydrolysis, so this approach is an efficient method for synthesizing α -(*N*-sulfonyl)amino secondary amides.⁷

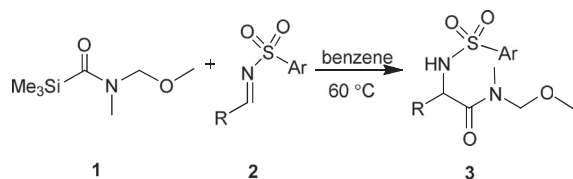
Results and discussion

N-Sulfonylimines **2** were easily prepared by the reaction of aldehydes and benzene sulfonicamide or *p*-methylbenzene sulfonicamide,⁸ which reacted with *N*-methoxymethyl-*N*-methylcarbamoyl(trimethyl)silane **1** in a benzene solution under anhydrous conditions, good to excellent yields of α -(*N*-sulfonyl) aminoamides **3** were obtained. Results are displayed in Table 1. However, *N*-sulfonylimines as the C=N substrates did not react with carbamoylsilane **1**. This result may be from the weaker electron-withdrawing ability of sulfinyl, and may reflect that the electronic property of the substituents on the C=N bond plays a significant role.

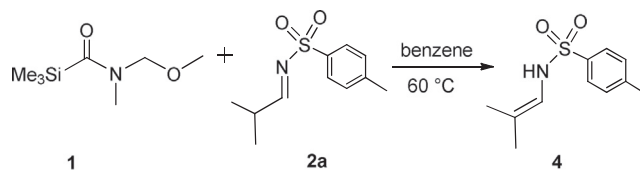
In an initial attempt, we selected aliphatic *N*-sulfonylimines, such as propyl or isopropyl *N*-sulfonylimine to react with equimolar amounts of carbamoylsilane **1**. It was found that no desired products were obtained, and carbamoylsilane **1** was completely consumed. To our surprise, when *N*-sulfonylimine **2a** reacted with carbamoylsilane **1**, the compound **4**, an isomer of **2a**, was isolated in 94% yield after 16 h at 25 °C (Scheme 2). We speculate that the

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Scheme 1. The reaction of *N*-methoxymethyl-*N*-methylcarbamoyl(trimethyl)silane **1** with *N*-sulfonylimines **2**.



Scheme 2. The isomerization of *N*-sulfonylimine **2a**.

Table 1
α-(*N*-Sulfonyl)aminoamides **3** from *N*-sulfonylimines **2** and carbamoylsilane **1**

Entry	<i>N</i> -Sulfonylimine	Product	Time ^a (h)	Yield ^{b,c} (%)
1			16	0
2			14	71
3			18	71
4			23	84
5			24	77
6			20	81
7			21	86
8			14	95
9			20	83
10			23	84
11			15	79

^a To complete consumption of carbamoylsilane **1** in benzene at 60 °C.

^b Isolated yield based on *N*-sulfonylimines. Characterization data are given.¹²

^c 1:1.1 mol ratio of *N*-sulfonylimines and carbamoylsilane.

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