



Synthesis of new imines and amines containing organosilicon groups

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ABSTRACT

The Peterson olefination reaction of terephthalaldehyde with tris(trimethylsilyl)methyl lithium, $(\text{Me}_3\text{Si})_3\text{CHLi}$, in THF at 0 °C gives 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (**1**) and 4,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene (**2**). The new aldehyde (**1**) reacts with variety of amines in ethanol to afford the corresponding imines (**3**) containing vinylbis(trimethylsilyl) group. The newly synthesized imines (**3**) can be completely converted into amines containing vinylbis(trimethylsilyl) group with an excess amount of NaBH_4 . In the case of N-[4-(2,2-bis(trimethylsilyl)ethenyl)benzyl]-2,6-dimethylaniline LiAlH_4 was used as a reducing agent in THF.

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1. Introduction

Vinylsilanes are useful reagents in organic synthesis because the C (sp^2)-Si bonds undergo numerous transformation [1]. Vinylbis (silanes), which show a number of similar properties, have received significant attention as potential synthons in organic and organo-silicon synthesis [2]. The potential of the vinylbis(silanes) as precursors for the preparation of ketones and isoxazoline derivatives, as well as a variety of important organosilicon reagents, such as acylsilanes, epoxy silanes, silanols, has stimulated their development. In contrast to vinyl silanes however, vinylbis(silanes) are relatively unexplored [3]. We have recently reported [4] new derivatives of vinylbis(silanes) via Peterson-type olefination reaction. However, no vinylbis(silanes) containing imine and amine group have hitherto been reported.

Imine, also known as azomethine, is formed by the reversible condensation between amine and carbonyl group. This reaction was discovered by the German chemist Hugo Schiff in 1864 and since then imines are also called as Schiff base [5]. An imine is a chemical compound containing carbon–nitrogen double bond with a general structure $\text{R}_1\text{R}_2\text{C}=\text{NR}_3$ used as a key intermediate for the synthesis of nitrogen heterocycles [6]. From the fundamental point of view, reduction of imines to the corresponding amines represent one of the most widely used and valuable functional group transformations in synthetic organic chemistry, since amines

constitute important precursors to compounds that are of such interest in pharmaceutical and agricultural industries [7,8].

In the present work, we describe the synthesis of some vinylbis (silane) derivatives containing imine and amine groups. The newly synthesized vinylbis(silanes) containing imine and amine group might be used for the preparation of heterocycles and other organic compounds containing organosilicon group, which cannot be achieved via other methods.

2. Results and discussion

Tris(trimethylsilyl)methane, $(\text{Me}_3\text{Si})_3\text{CH}$, has been conveniently prepared by the reaction of CHCl_3 and Li with Me_3SiCl in THF. The generation of $(\text{Me}_3\text{Si})_3\text{CHLi}$ was easily accomplished via deprotonation of $(\text{Me}_3\text{Si})_3\text{CH}$ by MeLi in THF [9,10].

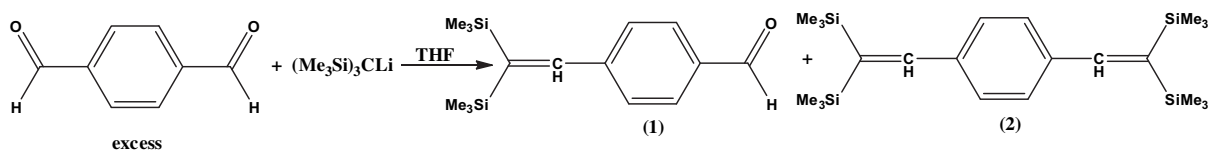
The precursor 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (**1**) was prepared from the reaction of terephthalaldehyde with [(trimethylsilyl)methyl]lithium, $(\text{Me}_3\text{Si})_3\text{CHLi}$, (Scheme 1).

In order to optimize the conditions for the formation of **1**, we decided to investigate the reaction of $(\text{Me}_3\text{Si})_3\text{CHLi}$ (1 equiv.) with various amounts of terephthalaldehyde at different temperatures (Table 1). When 5 equivalent of terephthalaldehyde was used at 0 °C, **1** was the major product.

The newly synthesized 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (**1**) was treated with an excess of various aromatic amines, the formation of the corresponding imines took place quite smoothly (Scheme 2). The reaction was performed in alcohol (methanol or ethanol) and was monitored via FTIR, actually, the infrared spectra of imines showed the expected absorptions in the

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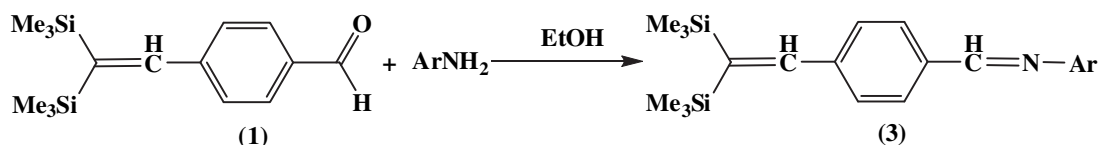
Scheme 1. The preparation of 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde via Peterson protocol.

Table 1

Summary of experimental conditions and yields obtained in the reaction of terephthalaldehyde with $(\text{Me}_3\text{Si})_3\text{CLi}$.

Entry	Terephthalaldehyde (equiv.)	$(\text{Me}_3\text{Si})_3\text{CLi}$ (equiv.)	Temperature	Condition	1 ^a (%)	2 ^a (%)
1	5	1	r.t	$(\text{Me}_3\text{Si})_3\text{CLi}$ was added dropwise over terephthalaldehyde and the reaction mixture was mixed for 15 h.	43	45
2	5	1	reflux	$(\text{Me}_3\text{Si})_3\text{CLi}$ was added quickly over terephthalaldehyde and the reaction mixture was mixed for 15 h.	33	55
3	5	1	r.t	$(\text{Me}_3\text{Si})_3\text{CLi}$ was added quickly over terephthalaldehyde and the reaction mixture was mixed for 15 h.	56	33
4	5	1	0 °C	$(\text{Me}_3\text{Si})_3\text{CLi}$ was added quickly over terephthalaldehyde and the reaction mixture was mixed for 30 min.	65	25

^a Isolated yields.



Scheme 2. The synthesis of imines containing vinylbis(trimethylsilyl) group.

range of 1550–1690 cm^{-1} usually attributed to $\text{C}=\text{N}$ stretching. In addition, the ^1H NMR spectrum of the raw product of the imines showed a complete disappearance of $-\text{CHO}$ at 9.99 ppm.

All the new synthesized imines (Table 2) were identified by GC–Mass method. In order to separate pure imines containing vinylbis(trimethylsilyl) group from the reaction mixture, preparative TLC was used. But in the presence of silica gel, the newly synthesized imines were converted to the precursor **1**.

So, we decided to apply direct reductive amination of imines which are attractive methods for the preparation of amine derivatives in organic synthesis [6].

Sodium borohydride, as a kind of common reducing agent, has been used widely in organic synthesis and there are several reports in the literature for reducing the imines by sodium borohydride [11–13].

We initially studied the reductive amination of the newly synthesized aldehyde (**1**) with aniline in ethanol, which afforded the corresponding imine (Scheme 3) that was then reduced with NaBH_4 to give the corresponding amine in 65%, isolated yield.

With the first successful result in hand, reduction of other imines with NaBH_4 was carried out under similar reduction conditions. The obtained results are presented in Table 3.

As shown in Table 3, high yield in the reduction of the imines was achieved in the presence of halogen (fluorine) functional groups. In the case of 2,6-dimethylaniline, reaction was not completed in the presence of NaBH_4 , so LiAlH_4 was used as the reducing agent in THF.

3. Conclusion

We demonstrated the convenient one-pot preparation of 4-[2,2-bis(trimethylsilyl)ethenyl]benzaldehyde (**1**) via Peterson protocol. When 5-fold the mol ratio of terephthalaldehyde was used at 0 °C, **1** was the major product.

The newly synthesized imines containing vinylbis(trimethylsilyl) group were obtained from the reaction of **1** with variety of amines. These imines might be used as intermediate for the synthesis of attractive molecules containing organosilicon group. The reaction of imines containing organosilicon groups with NaBH_4 gives the corresponding secondary amines containing organosilicon groups, which cannot be achieved via other methods.

4. Experimental

4.1. Solvent and reagents

Reactions involving organolithium reagents were carried out under dry argon. Solvents were dried by standard methods. Substrates for preparation of $(\text{Me}_3\text{Si})_3\text{CLi}$, viz., Me_3SiCl , Li, CHCl_3 and terephthalaldehyde, and also all amines used in synthesis of imines, NaBH_4 and LiAlH_4 were purchased from Merck and Fluka and used without further purification.

4.2. Spectra

The ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and with CDCl_3 as the solvent. The Mass spectra were obtained with a GC–Mass Agilent, quadrupole model 5973 N instrument, operating at 70 eV. The FTIR spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analysis were carried out with an elemental Vario EL III instrument.

4.3. Preparation of tris(trimethylsilyl)methylolithium, $(\text{Me}_3\text{Si})_3\text{CLi}$, in THF

The reagent was prepared as described by Grobel and co-workers [10].

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