

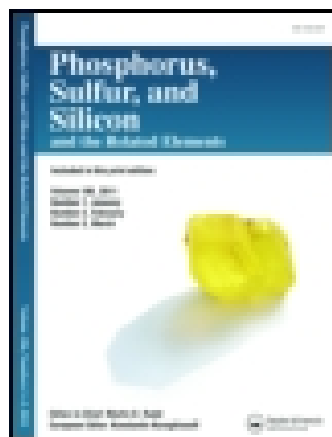
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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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Thiosilanes Based Delivery of Sulfur Functionalities in Organic Synthesis

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Published online: 23 Sep 2006.

To cite this article: Alessandro Degl'innocenti, Antonella Capperucci, Paola Ulivi, Alessandro Mordini, Gianna Reginato & Alfredo Ricci (1993) Thiosilanes Based Delivery of Sulfur Functionalities in Organic Synthesis, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 74:1-4, 385-386, DOI: [10.1080/10426509308038127](https://doi.org/10.1080/10426509308038127)

To link to this article: <http://dx.doi.org/10.1080/10426509308038127>

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THIOSILANES BASED DELIVERY OF SULFUR FUNCTIONALITIES IN ORGANIC SYNTHESIS.

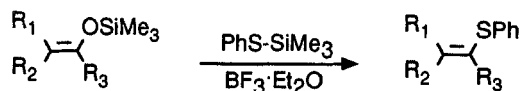
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Abstract: Thiosilanes have been proved efficient reagents in the transfer of sulfur functionalities onto organic substrates.

Vinyl sulfides have recently emerged as valuable synthetic intermediates¹, taking part in a number of interesting chemical transformations. Nonetheless, their synthesis is not straightforward, although a number of methodologies have been proposed in the literature². Moreover, 1,3-bisphenylthiopropanes have been shown extremely versatile intermediates, being used by Corey³ and Cohen⁴ for some key steps in the total synthesis of some prostaglandin and prostacyclin systems.

We report in this note on a novel synthetic approach to these classes of compounds⁵. We have found that upon treatment of a variety of silyl enol ethers in the presence of equimolar amounts of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ with different silyl sulfides, a clean reaction occurs, leading to the corresponding substituted vinyl derivatives as shown in Scheme 1.



$\text{R}_1, \text{R}_2, \text{R}_3, = \text{Alk}, \text{Cycloalk}, \text{Ar}.$

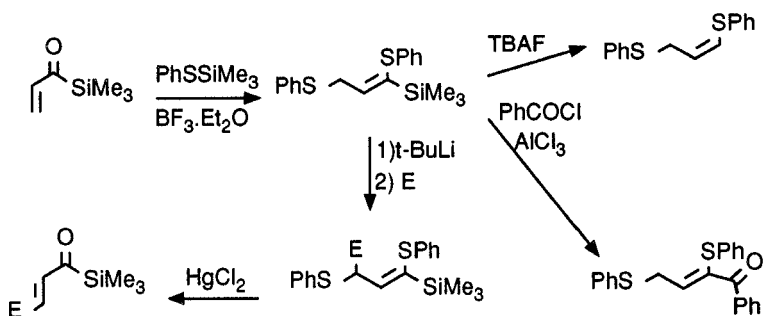
SCHEME 1

This reaction possesses a broad generality, occurring smoothly with different substrates, ranging from linear to cyclic enol ethers, leading to a wide variety of vinyl sulfides, a major advantage being the availability of silyl enol ethers from formally every carbonyl compound possessing an α hydrogen. Moreover, the reaction is regiospecific, as shown in the reaction of

6-methyl-1-cyclohexenyloxytrimethylsilane that affords 6-methyl-1-phenylthio-1-cyclohexene exclusively.

A further valuable extension of this reactivity may be achieved when reacting α -enones with 2 equivalents of PhSSiMe_3 . In this case, a direct and convenient entry to 1,3-bis-phenylthiopropanes can be achieved⁶.

When using propenoylsilane as the reacting enone, the corresponding silyl derivative may be obtained in a stereospecific fashion, and the C-Si bond further functionalized to more valuable compounds or simply desilylated with retention of configuration to afford a stereospecific access to 1,3-bisphenylthiopropane formally deriving from acrolein. Alternatively treatment with *t*-BuLi followed by quench with



SCHEME 2

different electrophiles yields functionalized silyl-bis-phenylthiopropanes which may be conveniently reacted with HgCl_2 to afford a general entry to variously functionalized propenoylsilanes (Scheme 2).

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