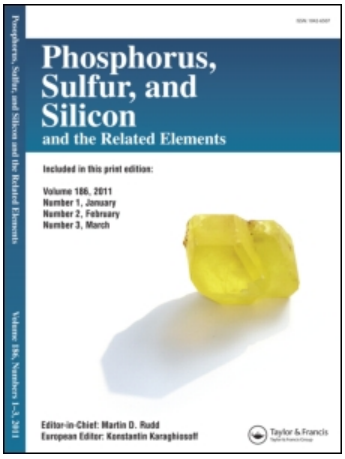

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Bonini, Bianca F. , Comes-Franchini, Mauro , Fochi, Mariafrancesca and Mazzanti, Germana(1997) 'New Chemistry of α-Silyl Vinylsulfides', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 451 — 452
To link to this Article: DOI: 10.1080/10426509708545593
URL: http://dx.doi.org/10.1080/10426509708545593

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 451–452
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New Chemistry of α-Silyl Vinylsulfides

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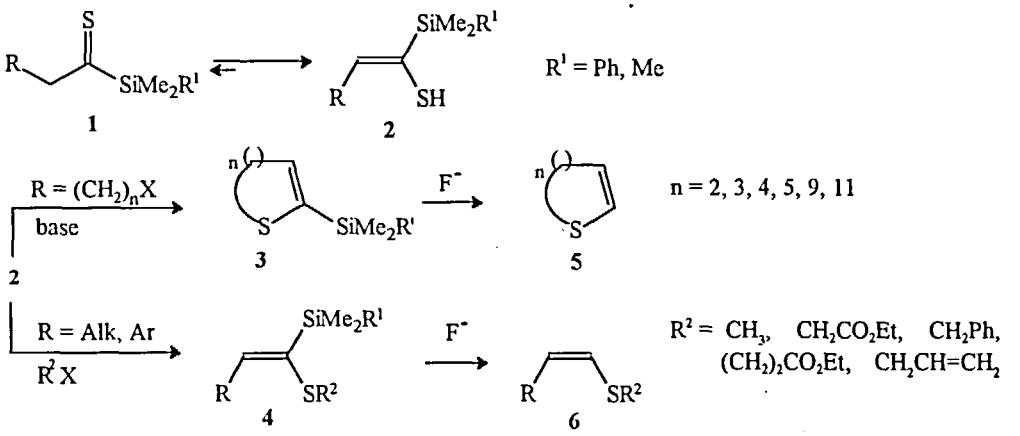
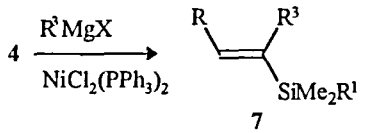
α-Silyl Vinylsulfides, obtained in a stereoselective manner through enethiolizable silyl thioketones, can be used for the synthesis of vinylsulfides and vinylsilane with a specific geometry, and for the prerarration of bicyclic and open chain thiofunzionalized enones.

KEY WORDS: α-silyl vinylsulfides, vinylsulfides, vinylsilane, cyclopentanones, enones.

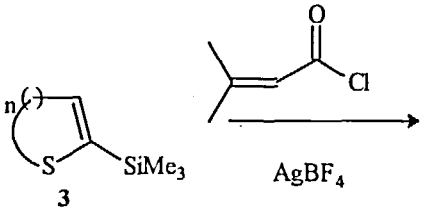
Several silylthioketones[1] have been synthetized and their chemistry investigated.The aliphatic derivatives **1** containing an α-hydrogen atom undergo enethiolization to Z α-silyl enethiols **2**.We found that **2** with R = $(CH_2)_nX$, (X = Halogen) undergoes ring closure to give cyclic Z-α-silyl vinylsulfides **3** for a range of ring sizes[2]. Compounds **2** with R = alkyl or aryl, react with a variety of halides R^2X to give open chain α-silyl vinylsulfides **4**. Protiodesilylation of **3** and **4** was achieved upon treatment with fluoride ion to give respectively cyclic vinylsulfides **5** and Z-vinylsulfides **6**, in good to quantitative yields.



Reaction of **4** with Grignard reagents, in the presence of an appropriate nickel catalyst, results in a series of vinylsilanes **7** with a definite geometry.

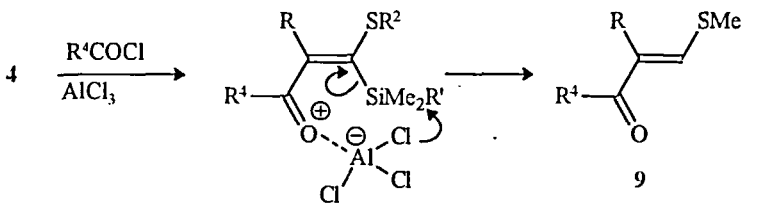


In α-silyl vinylsulfides **3** and **4**, the silyl and the thioether groups exert an opposed polarization on the olefinic bond.[3a,b] It is therefore of interest to study their reactions with electrophilic reagents. Compounds **3** (R^1 = Me), by treatment with β,β-dimethylacryloyl chloride in the presence of $AgBF_4$, gave bicyclic α,β-unsaturated ketones **8** in very good yields.



n	Yield (%)
2	83
3	90
4	92
5	91

Compounds **4**, when reacted with acylchlorides in the presence of $AlCl_3$, gave thiofunctionalized α,β-unsaturated ketones **9**. The formation of compounds **9** can be tentatively rationalized with an attack of the electrophile in the β-position, followed by desilylation assisted by the $AlCl_3$ coordinated with the carbonyl group *cis* to the silicon.



In conclusion the reaction of cyclic and acyclic α-silyl vinylsulfides with electrophiles is controlled by the sulfur in agreement with other results reported in the literature.[3a,b]

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