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New Chemistry of α -Silyl Vinylsulfides

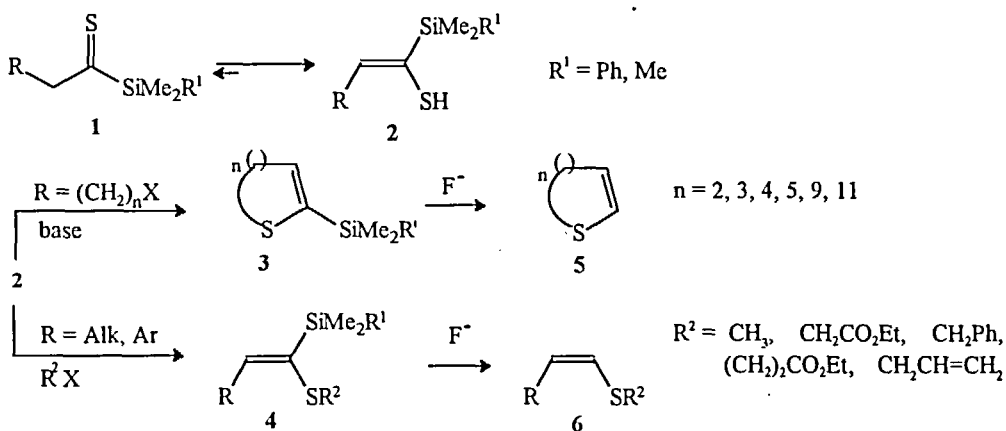
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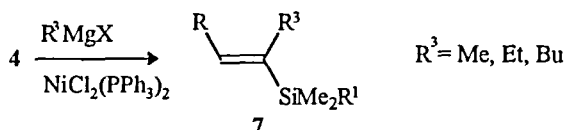
α -Silyl Vinylsulfides, obtained in a stereoselective manner through enethiolizable silyl thioketones, can be used for the synthesis of vinylsulfides and vinylsilane with a specific geometry, and for the preparation of bicyclic and open chain thiofunzionalized enones.

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

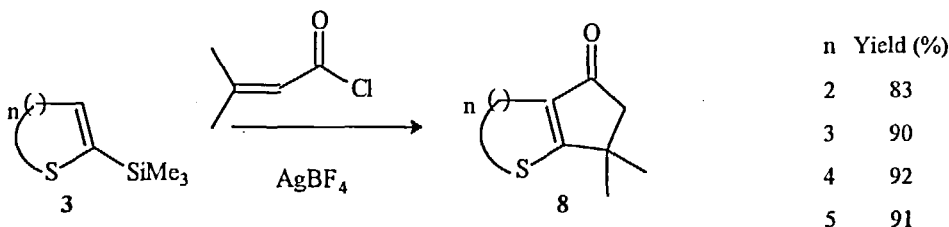
Several silylthioketones¹ have been synthesized and their chemistry investigated. The aliphatic derivatives **1** containing an α -hydrogen atom undergo enethiolization to *Z* α -silyl enethiols **2**. We found that **2** with $R = (CH_2)_nX$, ($X = \text{Halogen}$) undergoes ring closure to give cyclic *Z*- α -silyl vinylsulfides **3** for a range of ring sizes². Compounds **2** with $R = \text{alkyl or aryl}$, react with a variety of halides R^2X to give open chain α -silyl vinylsulfides **4**. Protodesilylation 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.



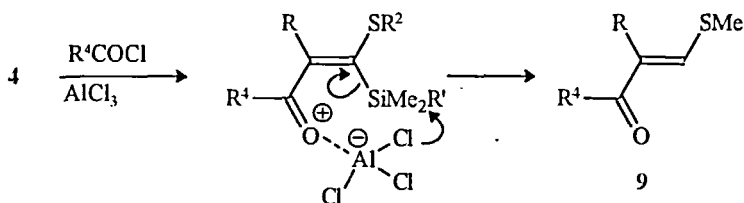
Reaction of **4** with Grignard reagents, in the presence of an appropriate nickel catalyst, results in a series of vinylsilanes **7** with a definite geometry.



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** ($\text{R}^1 = \text{Me}$), by treatment with β,β -dimethylacryloyl chloride in the presence of AgBF_4 , gave bicyclic α,β -unsaturated ketones **8** in very good yields.



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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