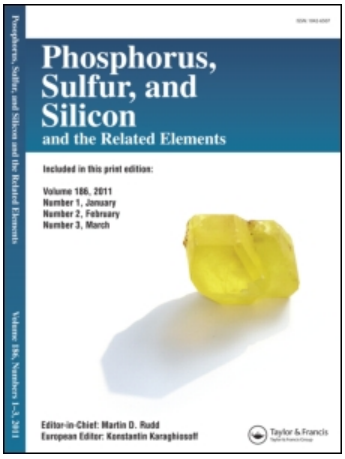

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Enethiolizable Thioacylsilanes as Intermediates for the Synthesis of Thietanols, Thiolanols, Thianols and Thiolactones

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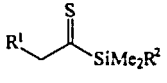
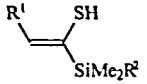
Thietanols, thiolanols and thianols can be obtained by a fluoride-mediated cyclization of Z-α-silyl vinyl sulphides containing a -carbonylic function in the chain bonded to the sulfur. The condensative cyclization of -carboxy-Z-α-silyl enethiols leads to unsaturated silylated thiolactones.

Keywords: Thietanols; thiolanols; thianols; thiolactones; α-silyl vinylsulfides

Thioacylsilanes are very attractive substances owing to their high reactivity, which allows the synthesis of a large variety of compounds containing the Si-C-S moiety.[1] Among thioacylsilanes the enethiolizable derivatives **1**, give quantitatively and stereoselectively Z-α-silyl enethiols **2** that can be transformed into Z-α-silyl vinylsulfides **3**. Both compounds **2** and **3** can be used for further synthetic purposes.[2a,b]



1



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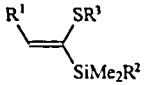
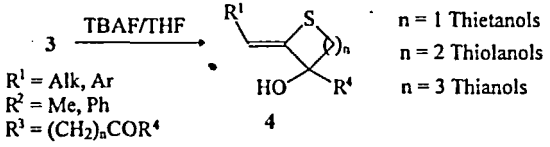
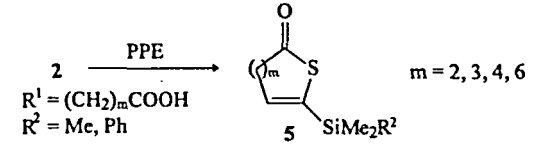


3

Z-α-Silyl vinylsulfides **3**, in which R^3 is a chain containing a ω-carbonylic function, give a fluoride-induced intramolecular cyclization to alcohols **4**, an almost unknown class of organosulfur compounds, characterised by the presence of both the alcoholic function and the exocyclic double bond.



The yields are very good (70-80%) in the cases of thietanols and thianols. The formation of thiolanols occurs with lower yields due to a competitive retro Michael reaction followed by a migration of a phenyl or a methyl group from the silicon to the adjacent carbon atom.[3] Substrates with $n > 3$ do not give the cyclic compounds but only the protiodesilylated derivatives. Z-α-Silyl enethiols **2**, containing a ω-carboxylic function in the R^1 chain, can be used for the synthesis of unsaturated silylated thiolactones **5**, through an intramolecular cyclization in the presence of polyphosphate ester (PPE) as a condensation reagent.



From these preliminary results, it stems that the combination of silicon and sulfur in the same molecule is an interesting subject of study. Further investigations of both the reactions are now in progress.

References

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[2] (a) B.F. Bonini, M. Comes Franchini, M. Fochi, G. Mazzanti, A. Ricci, *Tetrahedron Lett*, **53**, 7897 (1996). (b) B.F. Bonini, M. Comes Franchini, M. Fochi, G. Mazzanti, F. Peri, A. Ricci, *J. Chem. Soc., Perkin Trans. 1*, 2803 (1996).

[3] B.F. Bonini, M. Comes Franchini, M. Fochi, G. Mazzanti, A. Ricci, *J. Chem. Soc., Perkin Trans. 1*, 3211 (1997).