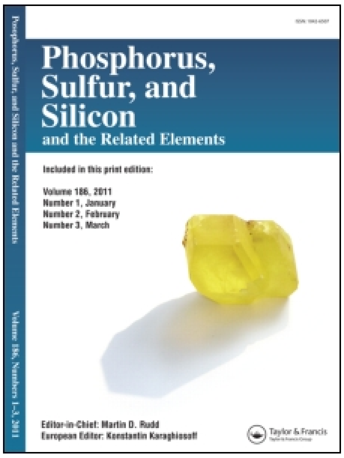

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Functionalized Sulfines

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FUNCTIONALIZED SULFINES

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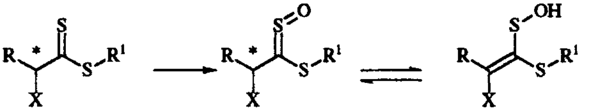
Sulfines (thione *S*-oxides)[1] are nonlinear sulfur-centered heterocumulenes with the general structure $R^1R^2C{=}S{=}O$. In this communication three aspects of functionalized sulfines are dealt with.

(I) Sulfines containing an α-hydrogen atom can undergo enethiolization to vinylsulfenic acids. Information about this tautomerization can be obtained by studying the chiral integrity of α-substituted sulfines. It was found that such sulfines derived from dithioesters with an α-methyl group (**1**) racemize very fast, whereas α-acetoxy- (**2**) and α-amino- (**3**) substituted sulfines retain their enantiomeric purity for a long period.

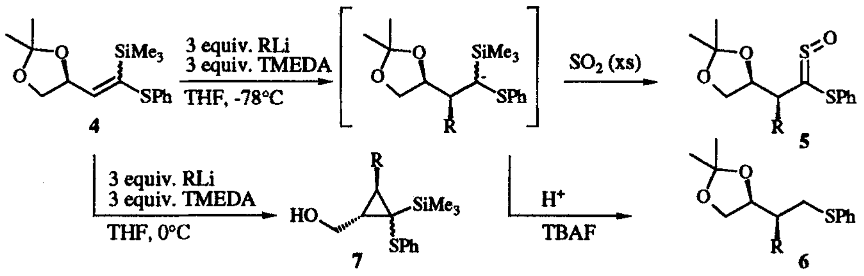


1 R = Ph, R^1 = Et, X = Me (*E*/*Z* = 0.7:1)
2 R = Ph, R^1 = Me, X = OAc (*E*/*Z* = 0.9:1)
3 R = Me_2CHCH_2, R^1 = Me, X = NHBoc (*E*/*Z* = 1:0)

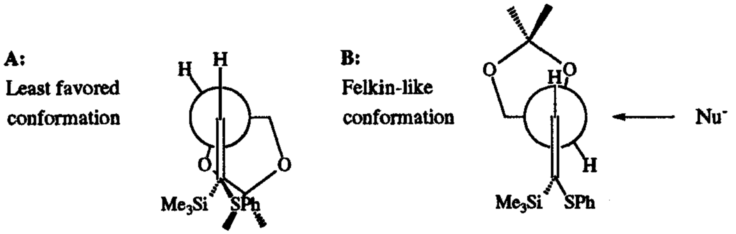
SCHEME 1

(II) Sulfines can be prepared conveniently by alkylidenation of sulfur dioxide using α-silyl carbanions[1]. Heteroconjugate addition of alkyllithium to vinylsilanes constitutes an interesting route to sulfine via this modified Peterson reaction. Starting from phenylthio-substituted vinylsilanes **4** derived from 1,2-*O*-isopropylidene D-glyceraldehyde functionalized sulfines were obtained as indicated in scheme **2**. These sulfines (**5**) were converted into the corresponding dithioacetal *S*-monoxides (overall yield 35%).

To study the stereochemistry of the heteroconjugate addition, the primary adduct was also quenched with a proton to give, after desilylation, product **6** consisting of one isomer only, implying that the addition of RLi had taken place in a stereospecific manner. An interesting



SCHEME 2

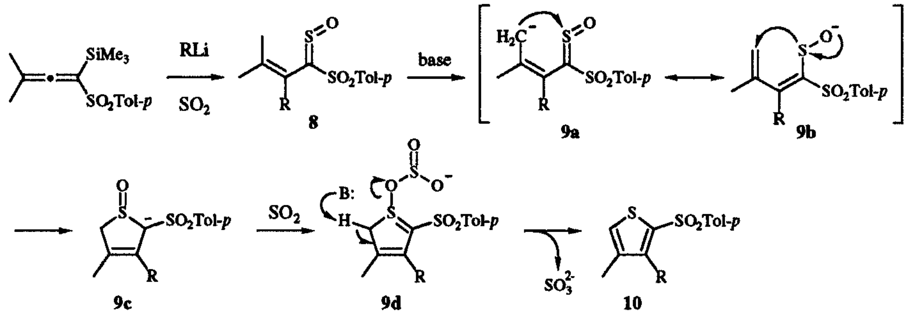


Energy difference between conformer A and B: ca 8 kcal/mol. (Calcd. by MM2)

FIGURE 1

observation was made when the heteroconjugate addition reaction was performed at 0°C instead of -78°C. Now an intramolecular ring closure had taken place to give cyclopropane derivatives **7**. The stereochemistry of **7** with an phenyl substituent was established by means of NOESY experiments. This stereochemical outcome can be explained by addition of alkyllithium to vinylsilane in a Felkin-Ahn fashion *i.e.* anti-addition to the preferred conformation **B** (Figure 1, energy calcd. by MM2) followed by an intermolecular substitution with inversion of configuration and concomitant expulsion of acetone.

(III) Heteroconjugate addition of alkyllithium to α-silyl allenyl sulfones followed by reaction with sulfur dioxide was expected to produce α,β-unsaturated sulfines. The actual products however, were thiophene derivatives as shown[2] in the scheme 3. The formation of these thiophenes **10** can be rationalized by assuming that initially an α,β-unsaturated sulfine **8** is formed as expected. Subsequent proton abstraction, with trimethylsilanolate acting as the base, from the γ-carbon atom of **8** leads to allylic anion **9a**, alternatively described in its mesomeric form **9b**. Intramolecular addition, which is conceivable from either mesomeric form of anion **9a,b**, leads to product **9c**. Aromatization and concomitant deoxygenation can be envisaged by invoking a reaction with excess of sulfur dioxide as pictured in structure **9d**. The elimination of SO_3^{2-} is reminiscent of a novel Pummerer-type rearrangement, induced by sulfur dioxide under basic conditions.



SCHEME 3

REFERENCES

1. B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **101**, 1 (1982) and *Phosphorus, Sulfur and Silicon*, **42**, 1 (1989).
2. S. Braverman, P.F.T.M. van Asten, J.B. van der Linden and B. Zwanenburg, *Tetrahedron Lett.*, **31**, 3867, (1991).