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# Phosphorus, Sulfur, and Silicon and the Related Elements

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# **Functionalized Sulfines**

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## **FUNCTIONALIZED SULFINES**

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Sulfines (thione S-oxides)<sup>1</sup> are nonlinear sulfur-centered heterocumulenes with the general structure R<sup>1</sup>R<sup>2</sup>C=S=O. In this communication three aspects of functionalized sulfines are dealt with.

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

$$R \underset{X}{\overset{\$}{+}} S^{-R^{1}} \xrightarrow{R} R \underset{X}{\overset{\$}{+}} S^{-R^{1}} \xrightarrow{R} R^{1}$$

- 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<sub>2</sub>CHCH<sub>2</sub>, R<sup>1</sup> = Me, X = NHBoc (E/Z = 1:0)

#### **SCHEME 1**

(II) Sulfines can be prepared conveniently by alkylidenation of sulfur dioxide using α-silyl carbanions<sup>1</sup>. 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

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  $\alpha$ -silyl allenyl sulfones followed by reaction with sulfur dioxide was expected to produce  $\alpha,\beta$ -unsaturated sulfines. The actual products however, were thiophene derivatives as shown² in the scheme 3. The formation of these thiophenes 10 can be rationalized by assuming that initially an  $\alpha,\beta$ -unsaturated sulfine 8 is formed as expected. Subsequent proton abstraction, with trimethylsilanolate acting as the base, from the  $\gamma$ -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.

SiMe<sub>3</sub> RLi 
$$SO_2$$
 Tol- $p$  base  $SO_2$ Tol- $p$   $SO_2$ Tol-

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