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ELIMINATIVE DEOXYGENATION: THE FACILE FORMATION OF α-TRIMETHYLSILYL VINYL SULFIDES FROM SULFOXIDES

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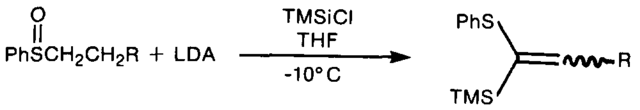
SUMMARY: Synthetically useful α-trimethylsilyl vinyl sulfides are generated in high yields by deoxygenation of the corresponding sulfoxides in the presence of excess LDA and trimethylsilyl chloride.

α-Trimethylsilyl vinyl sulfides are valuble intermediates which are finding increasing synthetic usage.[1] In spite of this synthetic potential, there are relatively few simple, high yield procedures available, particularly for the more highly substituted derivatives.[1h,2] We report here a facile procedure for the generation of α-trimethylsilyl vinyl sulfides in one step from readily available sulfoxide precursors.

Brook and Anderson[3] have reported that α-trimethylsilyl phenyl methyl sulfoxide, produced by the silylation of the respective anion, undergoes a facile migration of silicon to oxygen resulting ultimately in the formation of α-trimethylsiloxy thioanisole. In a related study, Vedejs and Mullins have described the preparation of a variety of α-trimethylsilyl sulfoxides and discussed their facile thermal rearrangements.[4]

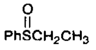
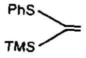
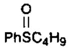
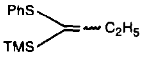
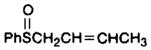
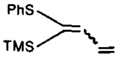
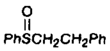
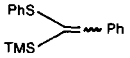
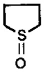
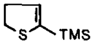
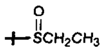
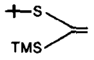
We have now found that the treatment of many sulfoxide derivatives with excess lithium diisopropyl amide (LDA) in THF in the presence of trimethylsilyl chloride produces in a single step the corresponding α-trimethylsilyl vinyl sulfides as shown below. The maximum yields were realized when the ratio of LDA/sulfoxide was ~3:1. Lower ratios produced more complex reaction mixtures while larger excesses did not markedly improve the yield of the desired products.



(I)

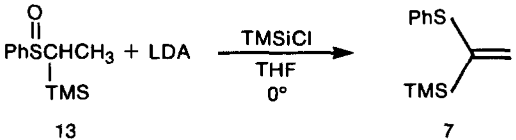
The reaction is quite general as shown by the examples in Table I.[5] The starting materials are readily available by the alkylation of the lithium salts of either thiophenol or t-butyl mercaptan followed by oxidation with sodium metaperiodate in ethanol-water. These thiols were chosen because of their ready availability, high nucleophilicities and the absence of α-hydrogens. The yields of the desired α-trimethylsilyl vinyl sulfides are good, and the products readily purified by chromatography over neutral alumina. In those cases where stereoisomers are possible, the product is isolated as a E/Z mixture with the E isomer predominating.[6] The procedure can be also used to prepare α-trimethylsilyl dienyl sulfides from unsaturated precursors such as 3.

Table I

Starting Materials	Products	E/Z[6] Ratio	Yield[a]
 $Ph\overset{\overset{O}{\parallel}}{S}CH_2CH_3$ 1	 7	—	75%
 $Ph\overset{\overset{O}{\parallel}}{S}C_4H_9$ 2	 8	2:1	80%
 $Ph\overset{\overset{O}{\parallel}}{S}CH_2CH{=}CHCH_3$ 3	 9	3:2	70%
 $Ph\overset{\overset{O}{\parallel}}{S}CH_2CH_2Ph$ 4	 10	3:1	75%
 5	 11	—	60%
 6	 12	—	75%

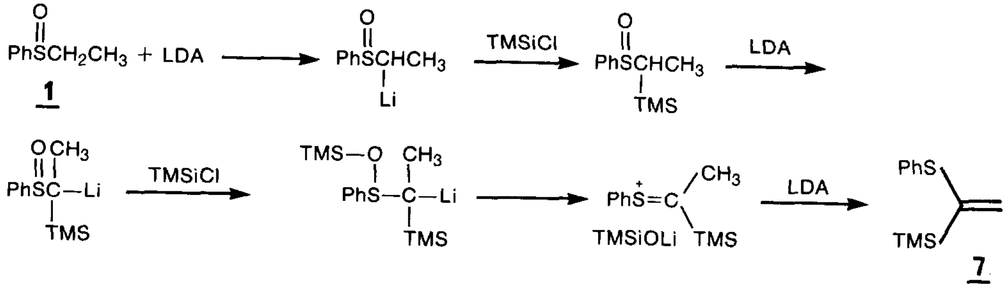
a. Yield of isolated product

The mechanism of this unusual transformation is of some interest. The observation that 1-thiophenoxyethylene rapidly yields 7 (70%) under the reaction conditions initially suggested that the vinyl sulfides themselves might be precursors to the α-trimethylsilyl vinyl sulfides. However, this facile silylation is not general, since more highly substituted derivatives often produce very complex mixtures under the reaction conditions. In this regard, <5% of the silylated product 8 was detected upon treatment of 1-thiophenoxy-1-butene as described.



13 7

The earlier work of Vedejs and others,[3,4] which showed that α-silylation of sulfoxide anions was facile, suggested that the corresponding α-trimethylsilyl sulfoxides might be involved in this transformation. Consistently, we have found that the α-trimethylsilyl sulfoxide 13 is cleanly transformed to 7 under our reaction conditions. On the basis of these observations, we propose the tenative mechanism shown below for more highly substituted sulfoxides. It is not known at this time whether the second silylation takes place directly on oxygen or on the α-carbon atom followed by rapid rearrangement under the reaction conditions. Previous studies have shown that such rearrangments can be quite rapid and the rates are structure dependent.[4]



In summary, it seems that α-trimethylsilyl vinyl sulfides can be prepared in good yield in one step by the silicon-assisted deoxygenation of sulfoxide derivatives. The chemistry of these silylated vinyl sulfides is under investigation.

GENERAL PROCEDURE FOR THE PREPARATION OF α-TRIMETHYLSILYL VINYL SULFIDES

A solution containing 2.0 mmol of the sulfoxide in 4 ml of dry THF was cooled to – 10°C and treated with 6.0 mmol of a freshly prepared solution of LDA. The deep yellow reaction mixture was stirred for 10m at –10°C and 12 mmol of distilled trimethylsilyl chloride was added in one portion. After warming slowly to 25°C, 10 ml of 5% sodium bicarbonate solution was added and the layers separated. The organic phase was washed with saturated salt solution and dried over potassium carbonate. The crude products were purified by column chromatography over neutral alumina using hexane as the eluant. The yield of isolated products ranged from 60-80%.

REFERENCES

1. (a) Magnus, P., Quagliato, D. A., and Huffman, J. C., *Organometallics*, **1982**, 1, 1240; (b) Magnus, P. and Quagliato, D. A., *Organometallics*, **1982**, 1, 1243; (c) Oda, H, Sato, M., Morizawa, Y., and Oshima, K., *Tet. Lett.*, **1983**, 24, 2877; (d) Ager, D. J., *J. Chem. Soc. Perkin Trans I*, **1983**, 1131; (e) Ager, D. J. , *Tet. Lett.*, **1983**, 24, 95; (f) Ager, D. J., *Tet. Lett.*, **1982**, 23, 1945; (g) Ager, D. J., *Tet. Lett.*, **1981**, 22, 587; (h) Cooke, F., Moerck, R., Schwindeman, O., and Magnus, P., *J. Org. Chem.*, **1980**, 45, 1046.
2. (a) Harirchian, B. and Magnus, P., *J.C.S. Chem. Comm.*, 1977, 522; (b) Gröbel, B.-T. and Seebach, D., *Chem. Ber.*, 1977, 110, 852; (c) Cookson, R. C. and Parsons, P. J., *J.C.S. Chem. Comm.*, **1976**, 990, and references cited therein.
3. Brook, A. G. and Anderson, D. G., *Can. J. Chem.*, **1968**, 46, 2115.
4. Vedejs, E. and Mullins, M., *Tet. Lett.* **1975**, 2017.

5. Consistent analytical and spectral data were obtained for all compounds.
6. The stereochemical assignments were based an the ^{1}HNMR chemical shift data[7] and are therefore tenative.
7. (a) Hojo, M., Masuda, R., and Takagi, S., *Synthesis*, 1978, 284; (b) Pretsch, E., Calec, Th., Seibl, J., and Simon, W., "Tabellen zur Strukuraufklarung Organischen Verbingungen," Springer-Verlag, 1976, New York, NY.

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