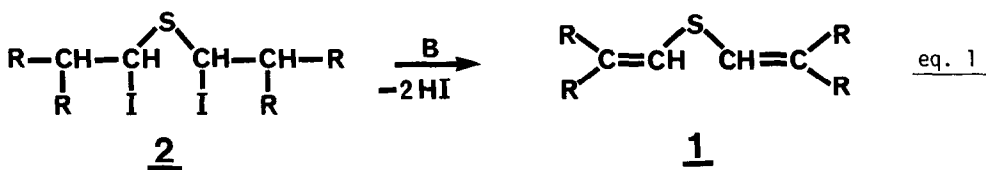


α, α' -DIODOSULFIDES
 A USEFUL PREPARATION OF DIVINYLIC SULFIDES

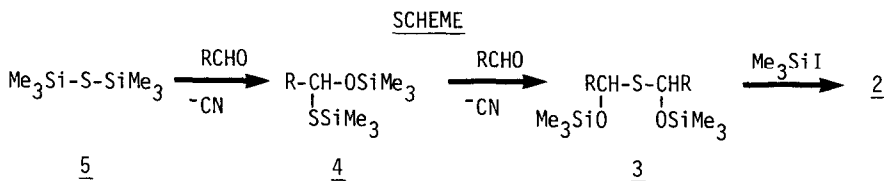
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Symmetric and unsymmetric divinyllic sulfides can be prepared almost quantitatively by the elimination of HI by base from the corresponding α, α' -diiodosulfide. These molecules are quantitatively formed in situ from α, α' -bis-trimethylsiloxy sulfides and iodo-trimethylsilane under mild conditions.

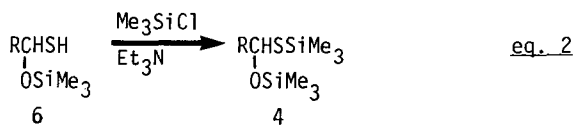
We have extended our earlier work¹ on the synthesis of vinylic sulfides to the construction of the divinyllic analogs for which a general preparation method has not been established.² A variety of symmetric and unsymmetric divinyllic sulfides (1) can be prepared almost quantitatively by the elimination of HI by base from α, α' -diiodosulfides (2) (eq. 1). These are formed in situ by the reaction of α, α' -bis-trimethylsiloxy sulfide (3) and iodo-trimethylsilane (4) under mild conditions.



Sym- α, α' -bis-trimethylsiloxy sulfides (3) can be prepared by using a modified procedure of



Evans³ from an excess of aldehyde and hexamethyldisilthiane⁴(5) in the presence of a catalytic amount of potassium cyanide in 18-crown-6-ether (Scheme). In this case the early stage of the reaction always showed the presence of 3 and 4 suggesting comparable rates for each step. As expected, this method was not effective for the preparation of unsym- α,α' -bis-trimethylsiloxysulfides(3). The problem was solved by preparing 4 from α -trimethylsiloxylthiol (6)^{5,6} (eq.2). By this path a number of sym and unsym- α,α' -bis-trimethylsiloxysulfides (3) were synthesized (Table I).



The preparation of di(1-trimethylsiloxy) butylsulfide (3a) is illustrative. A mixture of one equivalent of hexamethyldisilthiane (5) and 4 equivalents of butanal is placed in a sealed tube with ca. 5×10^{-3} equivalents of solid potassium cyanide-18-crown-6-ether complex. After sealing under argon, it is heated at 40° for two days. The product is purified by column chromatography (silica gel: hexane/CH₂Cl₂) or preparative GC.

All of these compounds showed reasonable stability and can be stored at room temperature for 2-3 months without decomposition. They all appear to be a mixture of diastereomers of nearly equal proportion according to ¹H-nmr.

Treatment of 3 with iodotrimethylsilane below 20°C quantitatively gave α,α' -diiodosulfides (2). This was easily detected by ¹H-nmr spectroscopy by following the chemical shift of the α -methine hydrogen as previously reported.¹ Efforts to isolate these α,α' -diiodosulfides (2) have not been successful. However, the addition of triethylamine to the solution expectedly gave the corresponding divinyllic sulfides (1) in high yield.

A general preparation of 1 is given as follows. To a dry dichloromethane solution (5.0 mL) of α,α' -bis-trimethylsiloxysulfide (3)(0.5 mol), iodotrimethylsilane (1.0 mol) is added dropwise at -78°C under a dry N₂ atmosphere. After 10 minutes stirring it is warmed to 0°C and stirred for an additional 10 minutes. To this solution, trimethylamine (1.1 mmol) is added dropwise at 0°C. The ice bath is removed and stirring is continued overnight. After solvent removal, the oily product is chromatographed by using silica gel with hexane as eluant. A number of divinyllic sulfides 1 can be prepared by this method and are summarized in Table II. The identification of these compounds was established by ¹H-nmr and mass spectrometry.

Acknowledgement

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6. A general procedure is given as follows. A dry ether solution of one equivalent of thiol, 1.5 equivalents of chlorotrimethylsilane and triethylamine is warmed at 40°C with stirring overnight under a dry nitrogen atmosphere. After collecting the triethylamine hydrochloride, the solvent is removed, and the residue distilled under reduced pressure.

	bp. (°C/mmHg)	H ¹ -nmr(δ, TMS in CCl ₄)
CH ₃ CH ₂ CH ₂ CH(OSiMe ₃)SSiMe ₃	53/0.8	4.94(t, J=6Hz, H), 2.0-0.7(m, 7H) 0.32(s, 9H, Me ₃ Si-S-), 0.15(s, 9H, Me ₃ Si-O-)
(CH ₃) ₂ CHCH(OSiMe ₃)SSiMe ₃	48/0.9	4.80(d, J=5Hz, H), 2.1-1.4(m, H) 0.95(d, J=6Hz, 6H), 0.30(s, 9H, Me ₃ Si-S-) 0.13(s, 9H, Me ₃ Si-O-)

TABLE I

Preparation of α,α'-bis-Trimethylsiloxysulfides

α,α'-bis-trimethylsiloxy sulfide 3 ^a	yield(%) ^b	H ¹ -nmr(δ, TMS in CDCl ₃)
a $\begin{array}{c} \text{Z} \quad \text{Z} \\ \quad \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH-S-CHCH}_2\text{CH}_2\text{CH}_3 \end{array}$	78	5.10 and 5.02(each t, J=5Hz, 2H) 2.1-0.7(m, 14H), 0.18(s, 18H)
b $\begin{array}{c} \text{Z} \quad \text{Z} \\ \quad \\ (\text{CH}_3)_2\text{CHCH-S-CHCH}(\text{CH}_3)_2 \end{array}$	73	4.86 and 4.74(each d, J=5Hz, 2H) 2.3-1.5(m, 2H), 0.96(d with shoulder, J=7Hz, 12H), 0.20(s, 18H)
c $\begin{array}{c} \text{Z} \quad \text{Z} \\ \quad \\ \text{C}_6\text{H}_{11}\text{CH-S-CHC}_6\text{H}_{11} \end{array}$	77	5.0-4.7(m, 2H), 2.1-0.8(m, 22H) 0.19(s, 18H)
d $\begin{array}{c} \text{Z} \quad \text{Z} \\ \quad \\ (\text{CH}_3)_2\text{CHCH-S-CHC}_6\text{H}_{11} \end{array}$	73	5.0-4.7(m, 2H), 2.2-0.8(m, 12H) 0.98(d, J=7Hz, 6H), 0.19(s, 18H)
e $\begin{array}{c} \text{Z} \quad \text{Z} \\ \quad \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH-S-CHC}_6\text{H}_{11} \end{array}$	76	5.2-4.6(m, 2H), 2.1-0.7(m, 18H) 0.18(s, 18H)

* Z = -OSiMe₃

^a The H¹-nmr spectrum showed a mixture of diastereomers.

^b The yields were determined by GC using an internal standard (SE-30 on Chromosorb-W).

TABLE II

Preparation of Divinylic Sulfides

Divinylic Sulfide <u>1</u>	yield(%) ^a	H ¹ -nmr(δ, TMS in CDCl ₃)	MS ^b m/e(rel.int.)
a <chem>CH3CH2CH=CH-S-CH=CHCH2CH3</chem>	88 ^c	6.3-5.3(m,4H), 2.5-1.9(m,4H) 1.00(t like,J=7Hz,6H)	142(10) 143(M+1,100)
b <chem>(CH3)2C=CH-S-CH=C(CH3)2</chem>	93	5.78-5.55(m,2H), 1.70(s with shoulder,12H)	142(27) 143(M+1,100)
c <chem>C1=CCCCC1-S-CH=C2CCCCC2</chem>	90	5.65(s,brd.,2H), 2.5-2.0(m,8H) 2.0-1.3(m,12H)	222(1) 223(M+1,100)
d <chem>(CH3)2C=CH-S-CH=C1CCCCC1</chem>	87	5.82-5.70(m,2H), 2.5-2.0(m,4H) 1.80(s with shoulder,6H) 2.0-1.3(m,6H)	182(1) 183(M+1,100)
e <chem>CH3CH2CH=CH-S-CH=C1CCCCC1</chem>	90 ^c	6.1-5.3(m,3H), 2.5-2.0(m,6H) 2.0-1.3(m,6H), 1.0(t,J=8Hz,3H)	182(3) 183(M+1,100)

^a Isolated yield (calculated on α,α'-bis-trimethylsiloxysulfide). Each was homogeneous by gas chromatography.

^b Chemical Ionization Mass Spectrometry.

^c Only the (E)-isomers were formed, (identified by GC and H¹NMR olefinic proton) cf. R. Muthukrishnan, and M. Schlosser, *Helv. Chim. Acta.*, 59, 13(1976).

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