

A FACILE PREPARATION OF VINYL SULFIDES¹

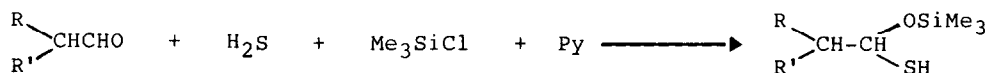
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Abstract: Vinyl sulfides are formed in high yield by the alkylation of trimethylsiloxy mercaptides.

Recently we developed a convenient preparation of vinyl sulfides *via* α -iodosulfides from the corresponding aldehyde and thiol². We now wish to report a more facile synthesis of vinyl sulfides from aldehydes and alkyl halides. Vinyl sulfides (enol thioethers) have been shown to be valuable synthetic intermediates³.

During the course of our studies on α -trimethylsiloxy sulfenyl compounds^{2,4}, we prepared α -trimethylsiloxy thiols (1) from aldehydes, H₂S and chlorotrimethylsilane in the presence of pyridine at room temperature^{4b} (Scheme 1).

Scheme 1



Thiol 1 smoothly reacts with NaH at 0°C generating H₂ in DMF under an argon atmosphere. This gives a slightly green solution which is very reactive towards alkyl halides affording vinyl sulfides in very good yield (Table 1).

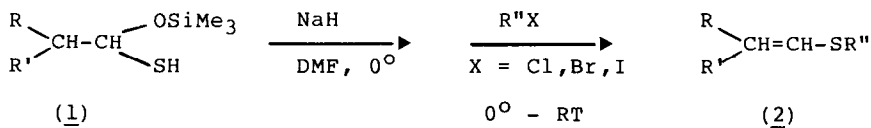
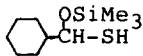
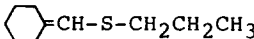
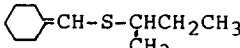

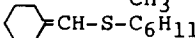
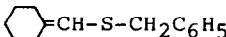
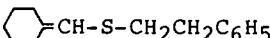


TABLE 1

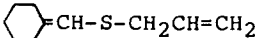
α -Trimethylsilyloxy Thiol (<u>1</u>)	R-X	Vinyl Sulfide ⁶ (<u>2</u>)	Yield (%) ^a
a) $\text{CH}_3\text{CH}(\text{OSiMe}_3)\text{-SH}$	$\text{PhCH}_2\text{CH}_2\text{Br}$	$\text{CH}_2=\text{CH-S-CH}_2\text{CH}_2\text{Ph}$	68
b) $(\text{CH}_3)_2\text{CH}(\text{OSiMe}_3)\text{-SH}$	$\text{PhCH}_2\text{CH}_2\text{Br}$	$(\text{CH}_3)_2\text{CH-S-CH}_2\text{CH}_2\text{Ph}$	91
c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OSiMe}_3)\text{-SH}$	$\text{PhCH}_2\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH-S-CH}_2\text{CH}_2\text{Ph}$	82 ^c
d) 	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$		77 89 90
e) <u>1d</u>	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}$		86
f) <u>1d</u>			84
g) <u>1d</u>	PhCH_2Br		85 ^b
h) <u>1d</u>	$\text{PhCH}_2\text{CH}_2\text{Br}$		90

^a Determined by VPC using an internal standard and based on 1.

^b Identified by comparison to an authentic sample.

^c Only one isomer was formed, but could not be unambiguously identified.

TABLE 2

Allyl Vinyl Sulfide	Yield (%) ^a	¹ HNMR (δ , CDCl ₃ , TMS) MS(M/e; rel.int.)
$\text{CH}_3\text{CH}_2\text{CH}=\text{CH-S-CH}_2\text{CH}=\text{CH}_2$	72	6.15-5.30(m, 3H olefinic), 5.30-4.95(m, 2H olefinic), 3.21(d, J=7Hz, 2H, -SCH ₂), 2.35-1.75(m, 2H), 0.98(t-like, 3H, J=8Hz); 128(M ⁺ 84), 99(42), 87(100), 85(73).
$(\text{CH}_3)_2\text{CH}=\text{CH-S-CH}_2\text{CH}=\text{CH}_2$	88	6.20-5.47(m, 3H olefinic), 5.30-4.90(m, 2H olefinic), 3.21(d, J=7Hz, 2H, -SCH ₂), 1.77(s with shoulder, 6H); 128(M ⁺ 100), 95(46), 87(76).
	86	6.60-5.40(m, 3H olefinic), 5.30-4.90(m, 2H, olefinic), 3.22(d, J=7Hz, 2H, -SCH ₂), 2.45-1.90(m, 4H), 1.80-1.30(m, 6H); 168(M ⁺ 65), 93(100), 127(67), 91(35).

^a Determined by VPC using an internal standard.

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6. ^1H NMR (δ , CDCl_3 , TMS); MS(m/e, rel. intensity): a 7.25(brd. S, 5H arom.) 6.60-6.15 (m, 1H olefinic), 5.32-5.00(m, 2H olefinic), 2.95 (S, 4H); 104(100), 105(45), 91(42): b 7.18(S, 5H arom.), 5.54(brd. S with fine structure, 1H olefinic), 2.82(\bar{S} , 4H), 1.73(S with shoulder, 6H); 192(M^+ 70), 101(100), 77(27), 59(26): c 7.28(brd. S, 5H aromatic), 6.15-5.40(m, 2H olefinic), 2.90(S, 4H), 2.50-1.80(m, 2H), 1.00(t-like, J= 8Hz, 3H); 192(M^+ 70), 105(100), 104(95), 101(82): d 5.56(brd. S with fine structure, 1H olefinic), 2.60(t-like, J= 7Hz, 2H $-\text{SCH}_2$), 2.45-1.90(m, 4H), 1.80-1.30(m, 6H), 0.98(t-like, J= 6Hz, 3H): e 5.68(brd. S with fine structure, 1H olefinic), 3.10-2.50(m, 1H $-\text{SCH}$), 2.50-1.90(m, 4H), 1.80-1.30(m, 8H), 1.30(d, J= 6Hz, 3H), 1.20-0.80(m, 3H); 198(M^+ 45), 95(100), 94(57), 127(56): f 5.65(brd. S with fine structure, 1H olefinic), 3.10-2.50 (m, 1H), 2.45-1.00(m, 20H); 210(M^+ 91), 128(100), 95(55), 94(43): g 7.35(S, 5H aromatic), 5.66(brd. S with fine structure, 1H olefinic), 3.83(S, 2H benzylic), 2.43-1.98(m, 4H), 1.70-1.30(m, 6H); 218(M^+ 7), 91(100), 92(13), 65(13), 93(10): h 7.30(S, 5H aromatic), 5.65(brd. S with fine structure, 1H olefinic), 2.00(S, 4H), 1.70-1.30(m, 6H); 232(M^+ 49), 93(100), 95(55), 94(43).

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