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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 $\underline{via} \ll -i$ 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 (<u>1</u>) from aldehydes, H₂S and chlorotrimethylsilane in the presence of pyridine at room temperature^{4b} (Scheme 1).

Scheme 1

$$R$$
 CHCHO + H₂S + Me₃SiC1 + Py - R CH-CH SH

Thiol <u>1</u> smoothly reacts with NaH at $0^{\circ}C$ 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).

$$\begin{array}{c|c} R & OSIMe_{3} \\ R' & CH-CH \\ SH \\ \hline DMF, 0^{\circ} \\ \hline X = C1, Br, I \\ \hline 0^{\circ} - RT \\ \hline (\underline{1}) \\ \hline 0^{\circ} - RT \\ \hline (\underline{2}) \end{array}$$

This method is also very effective for the preparation of a series of allyl vinyl sulfides of which the thio-Claisen rearrangement has been successfully applied to the synthesis of several natural products⁵ (Table 2).

This technique for the preparation of vinyl sulfides is general, although aryl halides cannot be alkylated; a typical procedure follows. To a dry DMF suspension of NaH (1.5 eq.), α -trimethylsiloxy thiol (1.0 eq.) is added dropwise at 0⁰C under an argon atmosphere. After 30 min of stirring, the cooling bath was removed. Stirring was continued for 10 min at room temperature and then alkyl halide (1.2 eq) was added dropwise to the resultant pale, green solution at 0^oC and stirred for 1 h. The reaction mixture was allowed to warm to room temperature. After 30 min, it was diluted with benzene and washed with water to remove DMF. The organic layer was separated and dried over anhydrous Na₂SO₄. Removal of solvent gave an oily material from which product was isolated by preparative VPC or column chromatography (silica gel-hexane/CH₂Cl₂).

A plausible mechanistic hypothesis for this alkylation reaction is indicated in Scheme 2. While it is possible that thioaldehydes (3) are produced as unstable intermediates, to date, efforts to trap them by addition of a diene have proved unsuccessful.



TABLE 1

\bigwedge -Trimethylsiloxy Thiol (<u>1</u>)		R-X	Vinyl Sulfide ⁶ (<u>2</u>)	Yield(%) ^a
a)	озіме _з Сн ₃ сн-ян	PhCH ₂ CH ₂ Br	CH ₂ =CH-S-CH ₂ CH ₂ Ph	68
b)	OSiMe ₃ (CH ₃) ₂ CH-SH	PhCH ₂ CH ₂ Br	(CH ₃) ₂ =CH-S-CH ₂ CH ₂ P	h 91
c)	OSiMe₃ CH₃CH₂CH₂CH-SH	PhCH ₂ CH ₂ Br	CH ₃ CH ₂ CH=CH-S-CH ₂ CH ₂	Ph 82 ^C
d)	OSiMe ₃ -CH-SH	$CH_3CH_2CH_2Br$ $CH_3CH_2CH_2C1$ $CH_3CH_2CH_2I$	_=сн-s-сн ₂ сн ₂ с	77 H ₃ 89 90
e)	<u>1d</u>	CH ₃ CH ₂ CH(CH ₃)Br	=сн-s-снсн₂сн	3 86
f)	<u>1d</u>	◯ -Br	\bigcirc =CH-S-C ₆ H ₁₁	84
g)	<u>1d</u>	PhCH ₂ Br	С = сн-s-сн ₂ с ₆ н ₅	85 ^b
h)	<u>1d</u>	PhCH ₂ CH ₂ Br	=сн-s-сн ₂ сн ₂ с	6 ^H 5 90
	a Determined by VPC b Identified by comp c Only one isomer war	using an internal arison to an authe s formed, but could	standard and based on ntic sample. d not be unambiguousl	<u>l</u> . y identified.
Allyl Vinyl Sulfide		TABLE 2 Yield(%) ^a	<pre>lhnmr (&,CDCl3,TMS) MS(M/e; rel.int.)</pre>	
сн ₃ сн ₂ сн=сн-s-сн ₂ сн=сн 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).	
(CH ₃) ₂ CH=CH-S-CH ₂ CH=CH ₂		88	6.20-5.47(m,3H olef 4.90(m,2H olefinic), 2H, -SCH ₂), 1.77(s w 6H); 128(M ⁺ 100), 95	inic), 5.30- 3.21(d, J=7Hz, ith shoulder, (46), 87(76).
	∕_=сн-s-сн ₂ сн=сн ₂	86	6.60-5.40(m,3H olefi (m,2H, olefinic), 3. 2H, -SCH ₂), 2.45-1.9 1.80-1.30(m, 6H); 16 93(100), 127(67), 91	nic),5.30-4.90 22(d, J=7Hz, 0 (m, 4H), 8(M ⁺ 65), (35).

^a Determined by VPC using an internal standard.

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- 6. H¹ NMR(\$\delta\$, CDCl₃, TMS); MS(m/e, rel. intensity): <u>a</u> 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): <u>b</u> 7.18(S, 5H arom.), 5.54(brd. S with fine structure, 1H olefinic), 2.82(S, 4H), 1.73(S with shoulder, 6H); 192(M⁺70), 101(100), 77(27), 59(26): <u>c</u> 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-1ike, J= 8Hz, 3H); 192(M⁺ 70), 105(100), 104(95), 101(82): <u>d</u> 5.56(brd. S with fine structure, 1H olefinic), 2.60(t-1ike, J= 7Hz, 2H -SCH₂), 2.45-1.90(m, 4H), 1.80-1.30(m, (m, 6H), 0.98(t-1ike, J= 6Hz, 3H): <u>e</u> 5.68(brd. S with fine structure, 1H olefinic), 3.10-2.50(m, 1H -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): <u>f</u> 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): <u>g</u> 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): <u>h</u> 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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