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α-IODOSULFIDES

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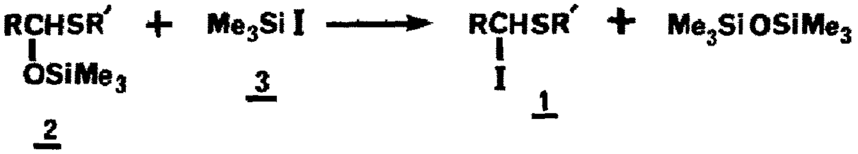
Abstract: *α-Iodosulfides are formed in high yield by the reaction of O-trimethylsilylhemithioacetals with iodotrimethylsilane. Elimination of HI by base from these α-iodosulfides provides easy access to vinylsulfides.*

Whereas the chemistry of α-chloro- and α-bromosulfides is well investigated because of the ready accessibility of these compounds by the halogenation of sulfides with N-chloro- or N-bromosuccinimides,[1] α-iodosulfides (1) are relatively rare compounds with no well defined method of preparation.[2] Their chemistry is virtually unknown.

We wish to report that a variety of α-iodosulfides (1) can be quantitatively prepared in situ under mild conditions from O-trimethylsilylhemithioacetals or ketals (2) and iodotrimethylsilane (3) (eq. 1). Since these acetals or ketals can be conveniently prepared from carbonyl compounds by the methods developed by one of us[3] and by Evans,[4] eq. 1 represents a simple route to obtain α-iodosulfides.

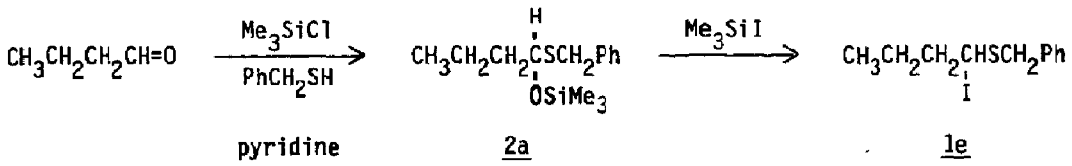


$$\underset{\underline{2}}{\underset{\mathrm{OSiMe_3}}{\underset{|}{\mathrm{RCHSR'}}}} + \underset{\underline{3}}{\mathrm{Me_3SiI}} \longrightarrow \underset{\underline{1}}{\underset{\mathrm{I}}{\underset{|}{\mathrm{RCHSR'}}}} + \mathrm{Me_3SiOSiMe_3} \qquad \text{eq 1}$$

The preparation of α-iodo-i-butyl phenylsulfide (1b) is illustrative. A dry $CDCl_3$ solution (1.0 mL) of α-trimethylsiloxy-i-butyl phenyl sulfide (2a, 127 mg, 0.5 mmol) in an NMR tube capped with a rubber septum was flushed by dry N_2 and cooled to -78°. A solution of trimethyliodosilane (100 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL) was injected dropwise by a syringe into the NMR tube. After 10 minutes at -78°, the mixture was allowed to warm to 0°C and stand for 2 minutes in an ice bath. The NMR spectrum of the sample clearly showed the formation of the α-iodosulfide 1a and the complete disappearance of the starting material 2a. The quantitative formation of hexamethylsiloxane was indicated by the NMR spectrum and was confirmed by preparative GC isolation and comparison with an authentic sample.

The advantage of the present method is that the iodo group can be introduced specifically to one of the alkyl groups of an unsymmetrical sulfide. This is illustrated by the preparation of α-iodobutyl benzyl sulfide (1c) (Scheme 1). The conventional method of NBS, NCS or I_2 halogenation of sulfides would undoubtedly have introduced the halogen into the more reactive benzylic position.[1b]

Scheme 1

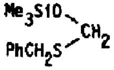
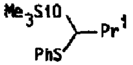
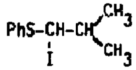
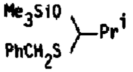
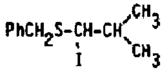
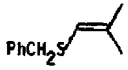
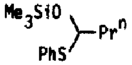
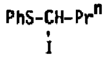
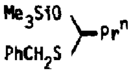
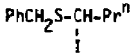
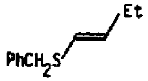
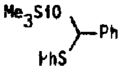
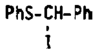
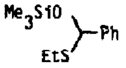
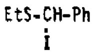
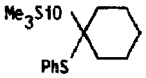
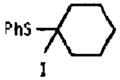
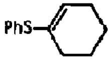
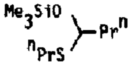


$$CH_3CH_2CH_2CH{=}O \xrightarrow[\substack{PhCH_2SH \\ \text{pyridine}}]{Me_3SiCl} \underset{\textbf{2a}}{CH_3CH_2CH_2\overset{H}{\underset{OSiMe_3}{C}}SCH_2Ph} \xrightarrow{Me_3SiI} \underset{\textbf{1e}}{CH_3CH_2CH_2\underset{I}{C}HSCH_2Ph}$$

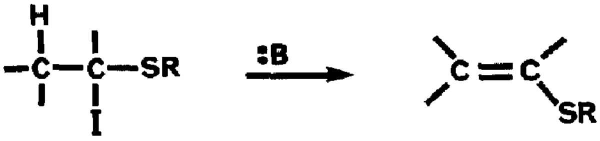
A number of α-iodosulfides have been prepared by this method including the unsubstituted α-iodomethyl benzyl sulfide (1a). In all cases, efforts to isolate these α-iodosulfides have not been successful. Their stability in chloroform solution were however reasonable so that they can be kept at room temperature for an hour or so. The α-iodobenzyl sulfides are somewhat less stable. They decomposed at room temperature within 20 minutes.

That 1a exists as a covalent compound and not the alternative possibility of an ionic structure is evident from the coupling and chemical shift of the α-methine hydrogen (Table 1). Thei formation was further confirmed by conversion to derivatives on reaction with sodium methoxide. For α-iodosulfides having no hydrogen β- to the iodo group, α-methoxysulfides were obtained, whereas α-iodosulfides with a β- hydrogen quantitatively gave vinylsulfides.[5] The elimination of HI to give vinylsulfides can also be accomplished with triethylamine, or phase-transfer

TABLE

O-Trimethylsilyl-Hemiacetal or Ketal[a]		α-Iodosulfide[b]	Yield (%)[c]	H^1 NMR (δ CDCl$_3$ TMS)	Vinylic Sulfide[g]	Yield (%)[e]	H^1 NMR (δ CDCl$_3$ TMS)
	a	$PhCH_2SCH_2I$	> 90	7.32 (s, 5H), 4.15 (s, 2H), 3.80 (s, 2H)			
	b		> 90	7.60-7.10 (m, 5H), 5.37 (d, J = 3 Hz, H), 0.95 (d, J = 6 Hz, 6H)		92	7.20 (brd. s, 5H), 6.50-5.20(m,H), 1.88 (s, 3H), 1.89 (s, 3H)
	c		> 90	7.30 (brd. s, 5H), 4.82 (d, J = 3 Hz, H), 3.73 (s, 2H), 2.00-1.25 (m, H), 0.93 (d, J = 6 Hz, 6H)		94	7.37 (brd. s, 5H), 6.20-5.00(m,H), 3.78 (s, 2H), 1.75 (s, 3H), 1.73 (s, 3H)
	d	 $\underset{\mathrm{I}}{\mathrm{PhS{-}CH}}{-}\mathrm{Pr}^n$	> 90	7.40 (m, 5H), 5.30 (t, J = 7 Hz, H), 2.40-1.25 (m, 4H), 0.93 (t-like, J = 7 Hz, 3H)	 (E) ~100%[f]	95	7.29 (brd. s, 5H), 6.30-5.57 (m, 2H), 2.52-1.90 (m, 2H), 1.05 (t, 3H, J = 7 Hz)
	e	 $\underset{\mathrm{I}}{\mathrm{PhCH_2S{-}CH}}{-}\mathrm{Pr}^n$	> 90	7.40 (s, 5H), 4.96 (t, J = 6 Hz, H), 3.90 (brd. s, 2H), 2.40-1.20 (m, 4H), 0.93 (t-like, J = 7 Hz, 3H)	 (E) ~100%[f]	92	7.30 (brd. s, 5H), 6.20-5.30 (m, 2H), 3.84 (s, 2H), 2.35-1.80 (m, 2H), 0.94 (t, 3H, J = 7 Hz)
	f	 $\underset{\mathrm{I}}{\mathrm{PhS{-}CH}}{-}\mathrm{Ph}$	> 80	7.70-7.20 (m, 10H), 6.23 (s, H)			
	g	 $\underset{\mathrm{I}}{\mathrm{EtS{-}CH}}{-}\mathrm{Ph}$	> 80	7.70-7.10 (m, 5H), 6.05 (brd. s, 2H), 2.62 (q. J = 8 Hz, 2H). 1.28 (t, J = 7 Hz, 3H)			
	h		> 90[d]	7.80-7.30 (m, 5H), 2.30-1.30 (m. 10H)		92	7.20 (brd. s, 5H), 6.10-5.80(m,H), 2.35-1.90 (m, 4H), 1.90-1.45 (m, 4H)
	i				 (E) ~100%[f]	86	6.10-5.30 (m, 2H), 2.65 (brd. t, 2H), 2.35-1.15 (m, 4H), 1.00 (t, 3H, J = 8 Hz)

conditions (aqueous NaOH and quaternary ammonium salt) or with an anion exchange resin (Rexyn 20). In cases where geometric isomers were possible, the vinylsulfides obtained always



were of the E- geometry.

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Footnotes for Table

[a] O-Trimethylsilylhemiacetals were prepared by two methods (refs. 3,4). [b] The reactions were carried out in an NMR tube using CDCl$_3$ solution (*ca.* 0.5 M): (2a) (ref. 4); H^1-NMR 7.29 (brd. s, 5H), 4.66 (s, 2H), 3.81 (s, 2H), 0.17 (s, 9H); (2b) (ref. 3); 7.62-7.15 (m, 5H), 4.90 (d, J = 6 Hz, H), 2.30-1.45 (m, H), 1.02 (d, J = 7 Hz, 6H), 0.0 (s, 9H); (2c) (ref. 4); 7.30 (brd. s, 5H), 4.55 (d, J = 7 Hz, H), 3.76 (s, 2H), 2.20-1.40 (m, H), 0.16 (s, 9H), 0.95 (d, J = 8 Hz, 6H); (2d) (ref. 3); 7.56-7.06 (m, 5H), 5.03 (t, J = 6 Hz, H), 1.96-0.67 (m, 7H), 0.0 (s, 9H); (2e) (ref. 4); 7.20 (brd. s, 5H), 4.80 (t, J = 6 Hz, H), 3.78 (s, 2H), 2.00-0.66 (m, 7H), 0.45 (s, 9H); (2f) (ref. 3); 7.70-7.15 (m, 10H), 6.18 (s, H); (2g) (ref. 3); 7.67-7.15 (m, 5H), 6.02 (s, H), 2.87-2.35 (m, 2H), 1.22 (t, J = 8 Hz, 3H), 0.14 (s, 9H); (2h) (ref. 3); 7.60-7.06 (m, 5H), 2.03-1.25 (m, 10H), 0.25 (s, 9H); (2i) (ref. 4); 4.86 (t, J = 6 Hz, H), 2.58 (t-like, J = 7 Hz, 2H), 2.00-0.70 (m, 12 H), 0.18 (s, 9H). [c] The yields were estimated from the comparison of H^1-NMR integration of the methyne proton bearing iodine as well as the aromatic protons. [d] The yield was estimated from that of the elimination reaction which was carried out by using Et$_3$N and gave the vinylic sulfide in 92% yield. [e] Isolated yield. [f] Only the (E) isomer was formed; it was identified by VPC analysis and PMR spectra (olefinic proton), cf. R. Muthukrishnan and M. Schlosser, Helv. Chim. Acta., 59, 13 (1976). [g] A weak infrared stretching band for the RSCH=CH- unit was observed at *ca.* 1620 cm^{-1}. In some cases this was hard to observe.

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2. G.E. Keyser, J.D. Bryant, and J.R. Barrio, Tetrahedron Lett., 3263 (1979).
3. T.H. Chan and B.S. Ong, Tetrahedron Lett., 319 (1976).
4. D.A. Evans, L.K. Truesdale, K.G. Grimm, and S.L. Nesbitt, J. Am. Chem. Soc., 99, 5009 (1977).
5. For a recent, thorough paper on the preparation and chemistry of vinylsulfides, see F.C. Cooke, R. Moerck, J. Schwindeman, and P. Magnus, J. Org. Chem., 45, 1046 (1980) and references cited therein.

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