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SYNTHETIC TRANSFORMATIONS USING TRIMETHYLSILYL IODIDE: THE GENERATION OF VINYL SULFIDES FROM SULFOXIDES

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SUMMARY: Treatment of sulfoxides with trimethylsilyl iodide in the presence of sterically hindered tert-amines results in facile eliminative deoxygenation with the production of the corresponding vinyl sulfides.

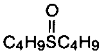
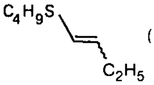
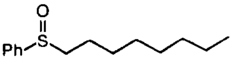
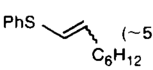
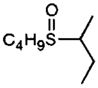
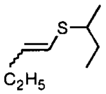
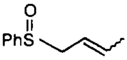
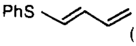
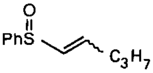
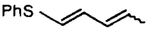
In recent years sulfoxide derivatives have become extremely important reagents for organic synthesis.[1] Accordingly, many new techniques have evolved which ultimately either remove the sulfoxide oxygen to regenerate the corresponding sulfide[2] or effect an oxidation of the α-carbon atom.[3] The latter procedure is a particularly valuable technique for modifying the functionality of the molecule.

We have recently reported that the use of electrophilic silicon derivatives in the presence of sterically hindered amine bases, particularly hexamethyldisilazane (HMDS), often leads to rapid α-deprotonation of carbonyl derivatives, as well as acetals and ketals to produce trimethylsilyl enol ethers[4a] and alkyl vinyl ethers, respectively.[4b,c] We report here that a similar reaction is observed for sulfoxides which results in an exceptionally mild procedure for the preparation of synthetically useful vinyl sulfides[5] under mildly basic conditions.

The treatment of dibutylsulfoxide 1 with two equivalents of TMSiI in the presence of excess HMDS led only to the rapid formation of iodine and dibutyl sulfide 6. In this regard, the presence of HMDS apparently had no effect on the reaction course, and simple deoxygenation[2] was observed. It was suspected that HMDS was too weak a base to effect deprotonation at a rate competitive with iodide displacement. This hypothesis was reinforced by the observation that the more vigorous base diisopropylethylamine (DIPEA) resulted in the rapid disappearance of 1 and the formation of the vinyl sulfide 7 in 75% yield. This product was produced as ~1:1 mixture of stereoisomers and no change in the isomer ratio was observed as the reaction time was varied from 0.5 to 24 hours.

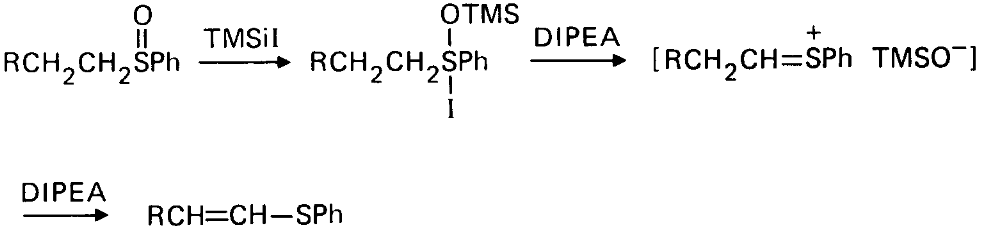
The eliminative deoxygenation of sulfoxides by TMSiI in the presence of tert-amine bases is quite general as demonstrated by the representative examples shown in Table I.

Table I

Starting Material	Reaction Conditions	Products	
 $C_4H_9\overset{O}{\overset{\|}{S}}C_4H_9$ 1	48h, 25°[a]	$C_4H_9SC_4H_9$ 6	(86%)[c]
	24h, 25°[b]	 7	(75%) (50:50)[d]
 2	1.5h, 25°	 8	(90%) (~50:50)[d]
 3	14h, 25°	 9	(81%) (67:33)[d]
 4	2.5h, 25°	 10	(85%) (>95% E)
 5	2h, 25°	 11	(91%)

a. 2.0 mmole TMSiI, 2.2 mmole HMDS, CH_2Cl_2; b. 2.0 mmole TMSiI, 2.2 mmole DIPEA, CH_2Cl_2; c. isolated yield; d. E/Z ratio

The formation of vinyl sulfides from the corresponding saturated sulfoxides is consistent with a base mediated deprotonation of the oxysulfonium salt, as shown below.



$$RCH_2CH_2\overset{O}{\overset{\|}{S}}Ph \xrightarrow{TMSiI} RCH_2CH_2\underset{I}{\overset{OTMS}{S}}Ph \xrightarrow{DIPEA} [RCH_2CH{=}\overset{+}{S}Ph\ \ TMSO^-]$$

$$\xrightarrow{DIPEA} RCH{=}CH{-}SPh$$

Interestingly, the steric demands of this deprotonation permit some selectivity in the transformation of unsymmetrical sulfoxides. In this regard, we noted that the reaction of 2-thiophenylbutane was incomplete even after 4 days at room temperature. The addition of excess reagent at this point led to the isolation of a complex mixture of products. In contrast, the reaction of 3 proceeded smoothly to yield an E/Z mixture of the corresponding vinyl sulfide 9. In this case, the product composition was spectrally and chromatographically identical to that generated by the free radical addition of sec-butyl mercaptan to 1-butyne in the presence of AlBN (70°C). This result confirms that the elimination proceeds most readily from the point of minimum branching which results in considerable regioselectivity.

All of the simple diakyl or alkyl aryl cases which we have examined generated E/Z product mixtures. While this was obvious from the complexity of the vinyl region in the ^{1}H NMR spectra, the isomers were not always separable by glpc for analysis. For those cases where assignment was not feasible by NMR or glpc techniques, the crude vinyl sulfide was reoxidized by sodium metaperiodate (ethanol-water) and the sulfoxides assigned by ^{1}H NMR using Eu(fod)$_3$ shift reagent. The E isomer was identified by the larger induced shifts of the β-olefinic protons and their larger vinylic coupling constants (J=15 versus 10 Hz for the Z isomers).[6]

Eliminative deoxygenation is even more rapid when allylic protons are present in either the α or γ positions (e.g., 4 and 5). In this regard, the product isolated from 4 in good yield was 1-thiophenyl-1,3-butadiene 10, which appeared essentially (>95%) as a single isomer. This material was easily oxidized to the corresponding sulfoxide which was identical to the major product isolated from the light induced, iodine catalyzed isomerization of Z-phenylsulfinyl-1,3-butadiene, as described by Ganoi.[7] The absence of the Z-isomer in the crude vinyl sulfide product was further assured by ^{1}H NMR analysis of the corresponding sulfoxide in the presence of Eu(fod)$_3$ and comparison with similar spectral data reported by Carey.[8] Although the dienyl sulfide 11 was clearly produced as an E/Z mixture, the exact composition could not be determined due to the complexity of the NMR spectrum of the oxidized mixture even in the presence of Eu(fod)$_3$. It thus seems that eliminative deoxygenation is also a facile route to phenylthio and phenylsulfinyl (via reoxidation) 1,3-butadienes which are materials of considerable synthetic interest.[9]

In summary, simple deoxygenation of sulfoxides by trimethylsilyl iodide can be prevented by the use of sterically hindered tert-amine bases and the products (vinyl and dienyl sulfides) are produced selectively, under mildly basic reaction conditions. The synthetic potential of this and related transformations is under investigation.

General Procedure for the Preparation of Vinyl Sulfides

One mmol of the sulfoxide was dissolved in 3 mL of methylene chloride containing 284 mg (2.2 mmol) of dry diisopropylethylamine (DIPEA). The mixture was cooled to 0°C under argon and 400 mg (2.0 mmol, 262 μL) of freshly distilled trimethylsilyl iodide was injected. The reaction mixture was slowly warmed to 25°C and the disappearance of the sulfoxide was monitored by TLC. After completion, the mixture was diluted with ether and washed with 2N H_2SO_4, 5% $NaHCO_3$ and dried over $MgSO_4$. The ether was removed and the vinyl sulfides distilled in a Kugelrohr apparatus.

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