## The Reaction of 2-Trimethylsilylethyl Sulfoxides with Sulfuryl Chloride. A Fragmentation Route to Sulfinyl Chlorides.

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Abstract: Sulfinyl chlorides were prepared in good to excellent yields by reacting aryl or alkyl 2-trimethylsilylethyl sulfoxides with  $SO_2Cl_2$ .

The term "abnormal Pummerer-type rearrangement" has been given to those reactions that involve electrophilic activation of a sulfoxide and the subsequent chemistry NOT leading to  $\alpha$ -oxidation of the sulfur containing substrate.<sup>1</sup> Some of the methods employed to avoid  $\alpha$ -oxidation process include blocking the  $\alpha$  site with substituents,<sup>1,2,4</sup> enhancing the acidity of the hydrogens at other nearby sites<sup>3</sup> or strategic placement of heteroatoms which can participate in fragmentation reactions.<sup>1,4,5</sup> We report herein that placing a 2-trimethylsilylethyl group on a sulfoxide precludes  $\alpha$ -oxidation and the fragmentation that occurs instead is useful for the preparation of sulfinyl chlorides.

The requisite sulfoxides were prepared by the radical addition of thiols to vinyltrimethylsilane (for one exception, see Table), followed by oxidation with  $NaIO_4(Rxn [1])$ . Reaction of the sulfoxides with sulfuryl chloride in  $CH_2Cl_2$  (-78°C r.t. over 3h) yielded the sulfinyl chlorides (Table). In all cases the reaction mixtures contained TMSCH<sub>2</sub>CH<sub>2</sub>Cl which could be removed under reduced pressure prior to distillation of the sulfinyl chloride. For the lower boiling sulfinyl chlorides (3e, f & i), the separation was difficult; the crude yields were actually ca. 80%. CAUTION: Although we did not encounter any problems, there is always a danger of explosion while distilling sulfinyl chlorides.<sup>6</sup> Good yields in all steps make the overall preparation an inviting one.

This method for the preparation of sulfinyl chlorides offers two advantages over many of the existing methods.<sup>5,6</sup> First there are no acidic byproducts such as HCl, acetic acid or acetyl chloride.



-	yields(%)			bp( <sup>o</sup> C)/mm	bp( <sup>o</sup> C)/mm <sup>lit.</sup>
R	1 <sup><i>a</i></sup>	2	$3^a$		
a Ph	84	98	90	62-63/0.04	71-73/1.5 <sup>6d)</sup>
b p-MeC <sub>6</sub> H <sub>4</sub>	75	100	94	79-80/0.01	79/0.0127
c p-ClC <sub>6</sub> H <sub>4</sub>	82	80	92	68-69/0.04	8,5
d 2-naphthyl	86	90	80 <sup>b,c</sup>	134-38/0.04	8,5
e n-Pr	80	95	61	22-23/1.0	66/12 <sup>6a)</sup>
f į-Pr	85	96	59	22-23/1.0	77/36 <sup>6a)</sup>
g PhCH <sub>2</sub>	73	100	94	84-88/0.01	
h TMS(CH <sub>2</sub> ) <sub>2</sub>	85	99	67 <sup>c</sup>	59-60/0.25	e
$i CH_2 = CHCH_2$	81 <sup>1</sup>	99	64	54-55/6.0	30/0.005 <sup>8</sup>
j c-C <sub>c</sub> H <sub>11</sub>	92	95	96	62-64/0.07	87/0.79
$k \underline{n} - C_{12} \dot{H}_{23}$	93 <sup>b,g</sup>	95	100	ß	<i>g</i> ,6d)

Table, The Preparation of Sulfinyl Chlorides,

Footnotes: "Yields after distillation unless otherwise reported. Ca. 100 mmol scale for 1 and ca. 30 mmol scale for 3. <sup>b</sup>Crude yield reported. <sup>c</sup>Decomposition occurred on distillation. <sup>d</sup>Bp not reported. <sup>e</sup>Satisfactory spectral data was obtained for 3h, a new compound. <sup>f</sup>Sulfide 1i was prepared from TMSCH<sub>2</sub>CH<sub>2</sub>SH and allyl bromide. <sup>g</sup>Not distilled.

These species often arise from other approaches to sulfinyl chlorides which involve the chlorination of thiol or sulfur acid derivatives. Second, this approach is a general preparation of sulfinyl chlorides from a sulfur species bearing a saturated carbon. The method allows one to carry a sulfur containing substrate through several preliminary reactions with the sulfur protected as a 2-trimethylsilylethyl sulfide or sulfoxide before generating the sulfinyl chloride at that sulfur. In their sulfide form, the precursor substrates possess considerable stability towards heat and aqueous acid and base.

We are currently investigating the reactions of other reagents with  $\beta$ -trimethylsilyl sulfoxides and sulfides to determine the generality of this type of fragmentation.

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