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FACILE REDUCTION OF SULFOXIDES BY DISILTHIANES

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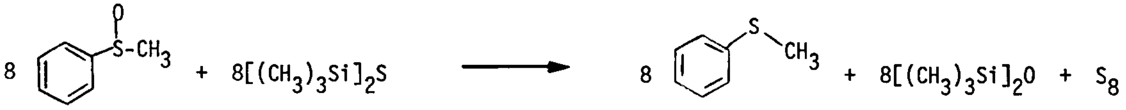
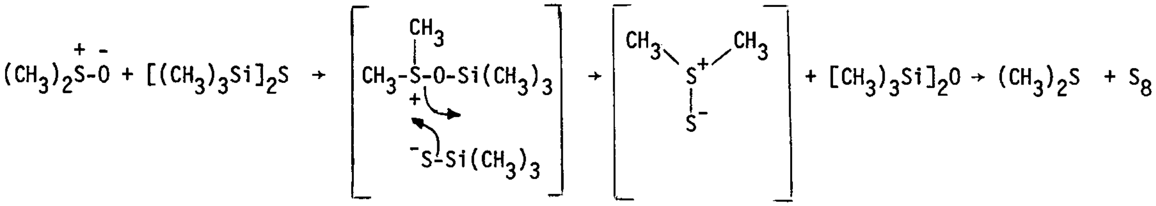
In recent years, organosilicon compounds have been utilized both as protecting groups and as reagents more and more frequently in synthetic organic chemistry.[1] The strength of the silicon-oxygen single bond provides a significant driving force for a number of these reactions such as the silyl-Wittig reaction[2,3] and the recently reported reaction of methylthiotrimethylsilane with ketones and aldehydes which yields the corresponding dimethylthioketals and hexamethyldisiloxane.[4] In this latter reaction, a weak Si-S bond (<u>ca</u>. 70 kcal/mol)[5] is converted to a strong Si-O bond (<u>ca</u>. 106 kcal/mol).[6] It should be noted that this latter reaction is one of the few applications of organosulfur derivatives of silicon to organic synthesis.

We should like to report that either hexamethyldisilthiane[7] or hexamethylcyclotrisilthiane[8] reacts with sulfoxides in chloroform, methylene chloride, or xylene solvents to give high yields of the corresponding sulfides, siloxanes, and elemental sulfur. Reduction of sulfoxides to sulfides has attracted considerable recent interest.[9-16] Among the advantages of this new method are generally quite high yields, mild reaction conditions (ambient temperature to 60°), usually rapid reaction rates, and neutral reaction conditions. Further, this method permits reduction of sulfoxides in the presence of other functional groups. Neither a neighboring β-keto nor an α-chloromethyl group are reduced by these disilthiane reagents. A β-keto group is not converted to a thiocarbonyl group by these reagents. On the other hand, the neighboring epoxide group in phenyl glycidyl sulfoxide reacts competively[17] with these disilthiane reagents resulting in only a moderate yield of phenyl glycidyl sulfide.[18] While neither hexamethyldisilthiane nor hexamethylcyclotrisilthiane are commercially available, they are easily prepared by well-worked out procedures: reaction of the appropriate chlorosilane with H_2S in the presence of pyridine.[8,19]



The mechanism of this deoxygenation is not at present certain. However, the following qualitative observations have been made. Hexamethylcyclotrisilthiane generally reacts faster with sulfoxides than does hexamethyldisilthaine. However, this reactivity order is reversed with dibenzyl sulfoxide. The reaction is sensitive to steric factors; thus dimethyl sulfoxide is reduced much more rapidly than dibutyl sulfoxide or any other sulfoxide we have examined. The reaction is also sensitive to the polarity of the solvent; thus reaction is considerably more rapid in chloroform or methylene chloride than in xylene. Finally, the observation that chloromethyl phenyl sulfoxide is reduced much more slowly than is methyl phenyl sulfoxide, (although the ultimate yields of sulfides in both cases are equally high), is consistent with the importance of nucleophilic attack by sulfoxide oxygen on silicon since the nucleophilicity of the sulfoxide oxygen of chloromethyl phenyl sulfoxide is lower due to the electronegative chlorine atom. It is tempting to propose that initial nucleophilic attack by sulfoxide oxygen on silicon leads to a siloxysulfonium cation/silyl sulfide anion pair which react further by a four center pathway leading to a siloxane and an unstable thiosulfoxide which decomposes to a sulfide and sulfur.



Experimental

All compounds are known with the exception of glycidyl phenyl sulfoxide. Known compounds had the physical and spectral properties in agreement with authentic samples or lit. values. Yields were determined by glpc using a 18 inch x 0.25 inch 20% polyphenyl ether on 60/80 chromosorb P column. Glycidyl phenyl sulfide yeilds were determined on a 18 inch x 0.25 inch 10% DC-QF1 on chromosorb W column. Glycidyl phenyl sulfoxide was prepared by oxidation of glycidyl phenyl sulfide with *m*-chloroperbenzoic acid using a two-phase solvent system[27] of CH_2Cl_2/aq. $NaHCO_3$ in 85% yield. It is extremely hygroscopic. It has the following physical and spectral properties: bp 146°/0.3 mm; nmr (CCl_4) δ 7.6-7.0 (m, 5H), 3.35-2.20 (m, 5H); ir S-O 1035 cm^{-1}. The exact mass of the parent ion was determined by high resolution mass spectrometry. Calcd. $C_9H_{10}O_2S$ 182.040; found 182.040.

Acknowledgements

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REDUCTION OF SULFOXIDE BY DISILTHIANE REAGENTS

Sulfoxide	Disilthiane	Solvent	Temp.	Time	Sulfide Yield		Siloxane Yield		Sulfur Yield
dimethyl sulfoxide[20]	A	none	10°	10 min.	97	dimethyl sulfide[20]	100	C	72
	B	xylene	10°	1 min.	80		57	D	81
dibutyl sulfoxide[20]	A	xylene	R.T.	10 hr.	94	dibutyl sulfide[20]	91	C	84
	B	xylene	R.T.	4 hr.	93		N.D.		96
methyl phenyl sulfoxide[21]	A	xylene	R.T.	10 hr.	90	methyl phenyl sulfide[20]	N.D.		100
	B	xylene	R.T.	2 hr.	89		N.D.		75
diphenyl sulfoxide[20]	A	$CHCl_3$	60°	10 hr.	100	diphenyl sulfide[20]	91	C	72
	B	xylene	R.T.	2 hr.	98		N.D.		100
dibenzyl sulfoxide[20]	A	CH_2Cl_2	R.T.	4 hr.	96	dibenzyl sulfide[22]	100	C	91
	B	CH_2Cl_2	R.T.	48 hr.	87		N.D.		N.D.
chloromethyl phenyl sulfoxide[23]	A	$CHCl_3$	R.T.	4 weeks	95	chloromethyl phenyl sulfide[24]	N.D.		N.D.
	B	$CHCl_3$	60°	36 hr.	100		N.D.		N.D.
ω-(methyl sulfinyl)-acetophenone[25]	A	$CHCl_3$	60°	10 hr.	65	ω-(methylthio)-acetophenone[26]	N.D.		N.D.
	B	$CHCl_3$	60°	10 hr.	55		N.D.		N.D.
glycidyl phenyl sulfoxide	A	$CHCl_3$	55°	18 hr.	45	glycidyl phenyl sulfide[7]	N.D.		N.D.
	B	$CHCl_3$	55°	10 hr.	35		N.D.		N.D.

A = hexamethyldisilthiane; B = hexamethylcyclotrisilthiane; C = hexamethyldisiloxane; D = mixture of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane; N.D. = Not Determined.

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