

FACILE DEOXYGENATION OF SULFOXIDES BY USING  
METAL/CHLOROMETHYLSILANES<sup>1</sup>

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Abstract—Deoxygenation of a various kind of sulfoxides including optically active one by Zinc/Dichlorodimethylsilane proceeds under very mild conditions to furnish the corresponding sulfides in high yields.

A number of significant developments on the synthetic methodology in organic sulfur chemistry have been undertaken so far, in particular, mainly for sulfoxides which being important intermediates in various transformation due to their activation characteristics of an adjacent C-H bond for alkylation and/or condensation, since recognition of the possibilities that sulfur compounds afforded for synthesis of non-sulfur types proceeded at ever swift pace. From this point of view, many kinds of reagents for the deoxygenation of sulfoxides to sulfides have been extensively explored as of now.<sup>2</sup>

In 1969, T.H. Chan et al.<sup>3</sup> reported that deoxygenation of aromatic sulfoxides with trichlorosilane to the corresponding sulfides proceeded in high yields. Under identical experimental conditions, however, benzyl and alkyl sulfoxides were transformed mainly to Pummerer-type products instead.

We paid our attention to their results and envisaged the following. 1. Substitution of Cl atom by methyl in chlorosilanes might be demonstrated so as to suppress both the affinities of Si atom toward oxygen atom to some extent and the formation of sulfur ylide. 2. Chlorosulfonium supposed to be an intermediate during deoxygenation should be rapidly reduced with an excess of metal powder. 3. An excess amount of chlorosilane is also deactivated by metal. As a result of a wide variety of the reaction conditions conducted, our idea has been realized. In order to find the optimum conditions for deoxygenation of methyl phenyl sulfoxide chosen as a

standard sulfoxide, effects of the silanes (trichloromethylsilane, dichlorodimethylsilane and chlorotrimethylsilane), powdered metals (Zn, Sn, Co, Ni and Fe) and dry solvents (acetone, dimethoxymethane, THF, methylene chloride, chloroform, ether, benzene and n-pentane) were systematically investigated. Consequently, the following appears to be the best combination upon consideration of the optimum yields, ready accessibilities and expenses of the reagents and the results obtained are summarized in the Table.

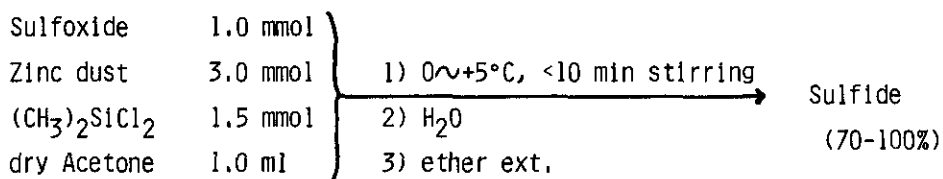
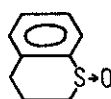
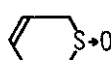
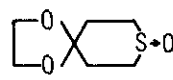
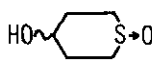
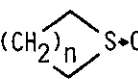
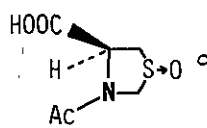
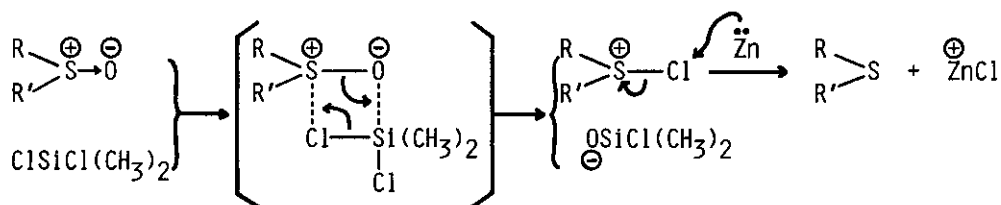


Table.<sup>a</sup> Deoxygenation of Sulfoxides with Zinc/Dichlorodimethylsilane

Sulfoxide	Sulfide <sup>b</sup>	Sulfoxide	Sulfide <sup>b</sup>
R-S(=O)-R'	Yield(%)		Yield(%)
CH <sub>3</sub>	CH <sub>3</sub>	85	
CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	83	
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	77	
Allyl	CH <sub>3</sub>	79	
Ph	CH <sub>3</sub>	93	
PhCH <sub>2</sub>	PhCH <sub>2</sub>	86	
Ph	Ph	quant.	
p-CH <sub>3</sub> -Ph	p-CH <sub>3</sub> -Ph	95	
p-Cl-Ph	p-Cl-Ph	quant.	
 S=O	n=1	70	 S=O <sup>c</sup>
	n=2	89	
	n=3	90	

a) Unless otherwise denoted, the reaction was carried out as follows. To a pre-cooled (0°C) suspension of sulfoxide and zinc powder in dry acetone was dropwise added dichlorodimethylsilane with stirring under argon. Within 10 min, ice-cold water (5 ml) was introduced and extracted with cold ether. Usual work-up of an ether extract gave sulfide in the yield recorded in the Table. b) All products showed satisfactory ir, <sup>1</sup>H-nmr, <sup>13</sup>C-nmr and mass spectral data. c) Colorless prisms, mp 187-188°C (decomp, EtOH/acetone), [α]<sub>D</sub><sup>25</sup> -115° (c 1.0, H<sub>2</sub>O).<sup>4</sup>

As can be seen in the Table, the following characteristics make this method advantageous. 1. Yields are usually high and in no cases were Pummerer-type products detected. 2. The reagents are readily accessible and of low cost. 3. Deoxygenation takes place under very mild conditions. 4. A kind of functional groups like hydroxyl, carboxyl, ketal and double bond, all can be tolerated as well in the reaction. 5. Racemization was never observed to any extent during deoxygenation. The plausible mechanistic pathway for this deoxygenation could be represented as follows.



## REFERENCES AND NOTES

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