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A Simple Preparative Method of Alkylthiotrimethylsilanes

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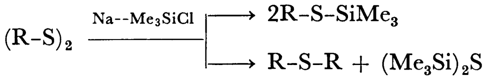
Synopsis. Treatment of *sym*-disulfides with metallic sodium in the presence of trimethylchlorosilane in an appropriate solvent affords the corresponding alkylthiotrimethylsilanes in high yield.

The utility of alkylthiotrimethylsilanes has recently been recognized. They can be efficiently used for conversion of the carbonyl group into the corresponding thioacetal or (1-alkylthioalkyl)trimethylsilanes.[1,2] Several methods have been developed, including silylation of lead mercaptides,[3] silylation of thiols with trialkylsilane catalyzed by transition metal[4] or with hexamethyldisilazane catalyzed by imidazole.[5]

In this paper we wish to describe a convenient method of preparation, starting from disulfides. As a part of studies on the reductive silylation reactions with metallic sodium and trimethylchlorosilane,[6] we have examined the reaction of disulfides with this reductive system.[7] *sym*-Disulfide was added to a solution of trimethylchlorosilane in an appropriate sodium suspension. After stirring or heating for an appropriate length of time, the substance deposited was filtered off. Removal of the solvent, followed by fractional distillation, afforded the corresponding alkylthiotrimethylsilane. By this procedure, various disulfides can be converted into the thiosilane derivatives, including primary, secondary, or tertiary alkyl, and phenyl groups, in high yield and with high purity.



$$(R\text{-}S)_2 \xrightarrow{Na\text{--}Me_3SiCl} \begin{cases} 2R\text{-}S\text{-}SiMe_3 \\ R\text{-}S\text{-}R + (Me_3Si)_2S \end{cases}$$

For the preparation of *n*-alkylthio derivatives, choice of solvent is important. Non-polar ones such as pentane or hexane should be used for efficient conversion. When ether was employed, the corresponding dialkyl sulfide was formed in sufficient amount along with alkylthiotrimethylsilane. For *s*- or *t*-alkylthio and phenylthio derivatives, ether can be used equally well as pentane, hexane and benzene.

In the cases of dimethyl and dibenzyl disulfides, carbon–sulfur bond cleavage took place predominantly or competitively and they could not be converted into the corresponding thiosilanes, giving instead, bis(trimethylsilyl) sulfide as the major product with any solvent. The reductive silylation procedure of dimethyl disulfide affords one of the most convenient methods for the preparation of bis(trimethylsilyl) sulfide,[8,9] since it can be isolated with high purity through simple fractional distillation.

$$(R\text{-}S)_2 \xrightarrow[R=CH_3 \text{ or } C_6H_5CH_2]{Na\text{--}Me_3SiCl} 2(Me_3Si)_2S + 2R\text{-}SiMe_3$$

Experimental

Materials. Disulfides were used after purification of commercial products by distillation. Trimethylchlorosilane was purified by distillation over CaH_2. Solvents were purified shortly before use by drying and distillation over sodium or sodium-benzophenone. Sodium dispersion was prepared in xylene in the usual way and used after complete removal of xylene.

General Procedure. Disulfide (17.5 mmol) and trimethylchlorosilane (4.2 g, 38.7 mmol) in an appropriate solvent (30 ml) was added to a sodium suspension (0.97 g, 0.422 g atom) in the same solvent (60 ml) over a period of 5 min at room temperature under argon atmosphere. After being stirred at room temperature or under refluxing for an appropriate time, the dark-purple colored reaction mixture was filtered through a pad of Celite and washed with the solvent (30 ml). The solvent was removed under atmo-

TABLE 1. REACTIONS OF *sym*-DISULFIDE, $(R\text{-}S)_2$, WITH $Na\text{--}Me_3SiCl$

R	Reaction conditions			Product (yield %, bp)
	Solvent	Temp	Period (h)	
CH_3[a]	ether	reflux	3	$(Me_3Si)_2S$[b] (67, 87—92°/80 Torr)
C_2H_5	pentane	R. T.	1	$C_2H_5SSiMe_3$[c] (83, 127—129 °C)
$(CH_3)_2CH$	pentane	R. T.	1	$(CH_3)_2CHSSiMe_3$[c] (80, 140—142 °C)
$(CH_3)_3C$	ether	R. T.	3	$(CH_3)_3CSSiMe_3$[c] (86, 155—159 °C)
	benzene	R. T.	2	$(CH_3)_3CSSiMe_3$ (72)
	hexane	R. T.	1	$(CH_3)_3CSSiMe_3$ (80)
n-C_6H_{13}	ether	R. T.	2	$C_6H_{13}SSiMe_3$[d] (60, 110—115 °C/30 Torr), $(C_6H_{13})_2S$ (30)
	benzene	reflux	1	$C_6H_{13}SSiMe_3$ (55), $(C_6H_{13})_2S$ (40)
	benzene	R. T.	9	$C_6H_{13}SSiMe_3$ (78)
C_6H_5	benzene	R. T.	0.5	$C_6H_5SSiMe_3$[c] (95, 120—122 °C/50 Torr)
$C_6H_5CH_2$[e]	benzene	reflux	3	$C_6H_5CH_2SiMe_3$ (50), $(Me_3Si)_2S$ (40)[f]

a) Carried out with Na (10 eq) and Me_3SiCl (10 eq). b) *Cf.* E. W. Abel, *J. Chem. Soc.*, **1961**, 4933. c) Ref. 4. d) *Cf.* J. D. Citron, *J. Organomet. Chem.*, **30**, 21 (1971). e) Carried out with Na (4.4 eq) and Me_3SiCl (4.0 eq). f) *Ca.* 50% of starting disulfide recovered.

spheric pressure and the residual oil was distilled, giving the corresponding thiosilane. The results are given in Table 1.

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