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### The Reactivity of Silylsulfides with Disulfides: A New Aspect of the Thiol-Disulfide Interchange

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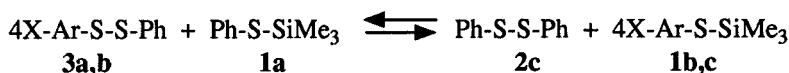
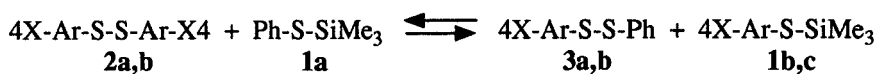
## The Reactivity of Silylsulfides with Disulfides: A New Aspect of The Thiol-Disulfide Interchange.

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In this communication we report the silylsulfide-disulfide interchange which can be considered a novel aspect of the well known and widely studied thiol-disulfide interchange.

The reaction of phenyl silyl sulfide **1a** with the diaryl disulfides **2a** and **2b** in CDCl<sub>3</sub> at 60 °C gave mixtures of symmetrical and unsymmetrical disulfides together with a new aryl silyl sulfide (Scheme 1).



**2a, 3a, 1b** : X=OMe

**2b, 3b, 1c** : X=Cl

Composition of the reaction mixtures was accomplished by <sup>13</sup>C nmr analysis monitoring the carbons atoms linked to sulfur in the various species. Relevant data are shown in Table 1.

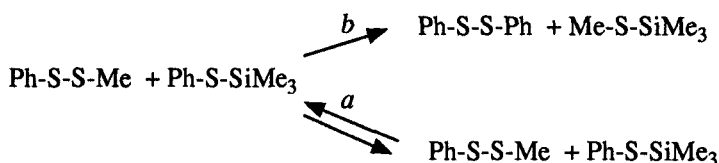
Similarly the reaction of **1a** with dimethyl disulfide gave rise to the exchange

Table 1. Composition of mixtures in the reactions of  
silyl sulfide **1a** with **2a** and **2b**

	X = OMe	X = Cl
4X-Ar-S-S-Ar-X4	42	28
Ph-S-SiMe <sub>3</sub>	32	21
4X-Ar-S-S-Ph	12	23
4X-Ar-S-SiMe <sub>3</sub>	11	23
Ph-S-S-Ph	3	5

reaction with formation of phenyl methyl disulfide and methyl silyl sulfide. On the contrary no exchange was observed in the reaction of methyl silyl sulfide with diaryl, dialkyl or aryl alkyl disulfides.

Surprisingly we couldn't detect any apparent reaction between phenyl silyl sulfide **1a** and phenyl methyl disulfide. However, using labelling experiments, it has been possible demonstrate that in the latter case a selective exchange had occurred (Scheme 2, path *a*).



This behavior has been also confirmed by the reaction of phenyl methyl disulfide with aryl silyl sulfides which, in any case, afforded phenyl silyl sulfide and aryl methyl disulfides exclusively.

The lack of reactivity showed by alkyl silyl sulfide towards disulfide might be due to the different  $d\pi-d\pi$  interactions between silicon and alkyl or arylthio residues.

The selectivity observed in the reaction of aryl silyl sulfides with aryl alkyl disulfides is likely due to the more enhanced leaving group ability of arylthio residues with respect to the alkylthio groups.