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UNEXPECTED SUBSTITUTION REACTIONS OF 1,3-DITHIETANE- 1,1,3,3-TETRAOXIDE (DISULPHENE)

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Abstract 1,3-Dithietane-1,1,3,3-tetraoxide ("disulphene") is a versatile reagent for the synthesis of sulphenes and sulphines¹. Upon investigating silylation reactions of disulphene (1) an unexpected O-silylation yielding a sulfoxoniumylide was found². The synthesis of more stable sulfoxoniumylides will be reported³.

Though disulphene (1) possesses acidic protons substitution reactions proceed only under weakly basic conditions. Undesired ring opening occurs in strong base and 1 is unreactive under acidic conditions (probably due to the lack of keto-enol-tautomerism in sulphones and the low solubility of 1). Upon reacting 1 with silyl-nonafluorobutane-sulphonates (nonaflates), extremely strong silylating reagents, we obtained the C-silylated derivatives 2a-d.

FIGURE I

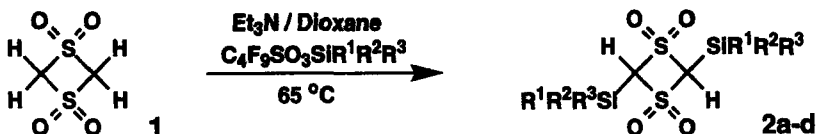


TABLE I Examples of ring-silylated products

	2a	2b	2c	2d
R ¹	Me	Et	^t Bu	ⁱ Pr
R ²	Me	Et	Me	ⁱ Pr
R ³	Me	Et	Me	ⁱ Pr

Using various nonaflates, a wide range of silylated disulphenes are accessible.

Attempts to further C-silylate the bis-silylated derivatives **2a-d** unexpectedly yielded the O-silylated derivatives **4a-d**.

FIGURE II

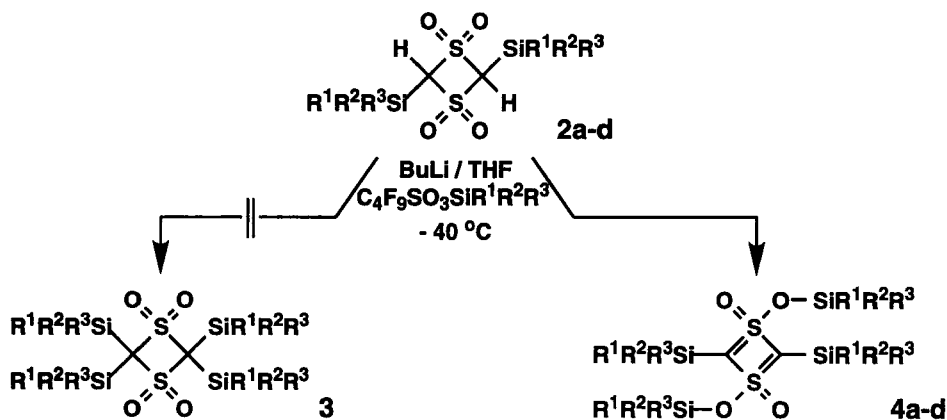


TABLE II Examples of O-silylated products

	4a	4b	4c	4d
R ¹	Me	Et	^t Bu	iPr
R ²	Me	Et	Me	iPr
R ³	Me	Et	Me	iPr

4a-d display characteristic ¹³C-NMR signals at 80 to 95 ppm for the ring carbon atoms and ²⁹Si-NMR signals at 27 to 30 ppm for O-Si and at -10 to -5 ppm for C-Si. These signals are consistent with the sulfoxoniumylide structure³.

The stability of **4a-d** increases with the size of the pendant silyl groups. **4a** and **4b** are unstable oils (even under argon at -78 °C) whereas **4c** and **4d** are stable powders, which can be readily characterized.

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