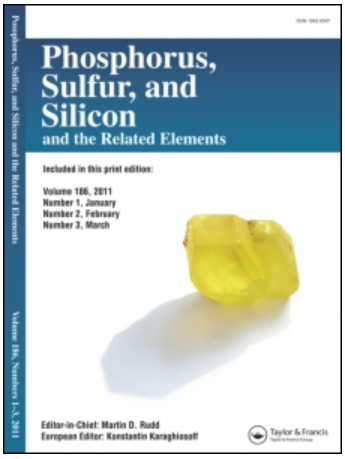

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Unexpected Substitution Reactions of 1,3-Dithietane-1,1,3,3-Tetraoxide (Disulphene)

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To cite this Article Sundermeyer, Wolfgang and Walch, Andreas(1994) 'Unexpected Substitution Reactions of 1,3-Dithietane-1,1,3,3-Tetraoxide (Disulphene)', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 477 — 478
To link to this Article: DOI: 10.1080/10426509408021911
URL: http://dx.doi.org/10.1080/10426509408021911

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 477–478
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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 sulphines[1]. Upon investigating silylation reactions of disulphene (**1**) an unexpected O-silylation yielding a sulphoxoniumylide was found[2]. The synthesis of more stable sulphoxoniumylides will be reported[3].

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), extremly strong silylating reagents, we obtained the C-silylated derivatives **2a-d**.

FIGURE I

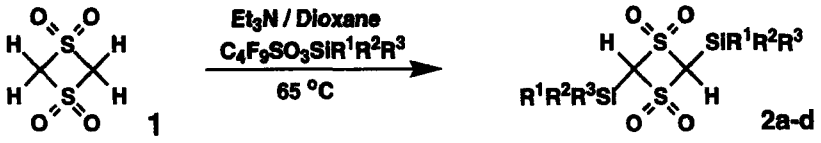

TABLE I Examples of ring-silylated products

	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

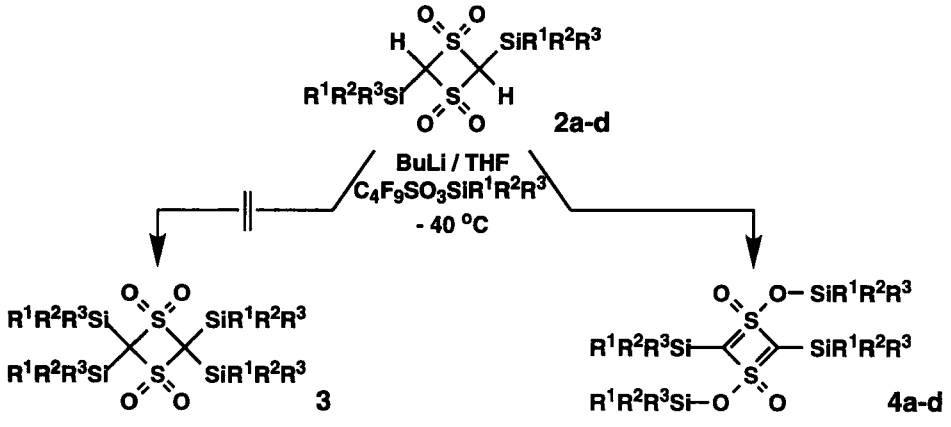

TABLE II Examples of O-silylated products

	4a	4b	4c	4d
R^1	Me	Et	^{t}Bu	^{i}Pr
R^2	Me	Et	Me	^{i}Pr
R^3	Me	Et	Me	^{i}Pr

4a-d display characteristic ^{13}C-NMR signals at 80 to 95 ppm for the ring carbon atoms and ^{29}Si-NMR signals at 27 to 30 ppm for O-**Si** and at -10 to -5 ppm for C-**Si.** These signals are consistant with the sulphoxoniumylide structure[3].

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.

REFERENCES

1. W. Sundermeyer, Synthesis, 349, (1988).
2. U. Rheude, W. Sundermeyer, Chem. Ber., 114, 3378, (1981)
3. W. Sundermeyer, A. Walch, Chem. Ber., 115, (1995), in press