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SILICON IN ORGANOSULPHUR CHEMISTRY. Part 2[1].
SYNTHESIS OF UNSYMMETRICAL DISULPHIDES

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Summary. Unsymmetrical aryl- and alkyl- disulphides are prepared from silylsulphides and thiosulphinates or thiosulphonates. Silyl sulphinic esters are also obtained in the reaction of the thiosulphonates.

Several methods are available in the literature for the synthesis of unsymmetrical disulphides.[2] However, most of them suffers from side reactions that cause randomization of the products, giving mixtures of symmetrical and unsymmetrical disulphides.

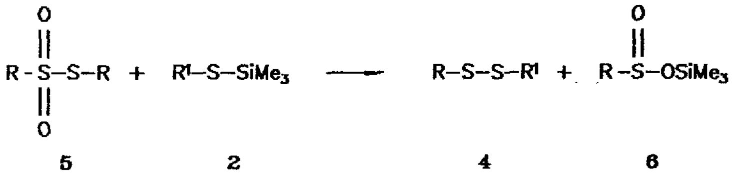
We report a new synthesis of unsymmetrical aryl- and alkyl- disulphides, occurring under neutral and mild conditions, which guarantee the lack of randomization processes.

The reaction of thiosulphinates 1 with methylthio or phenylthio trimethylsilane 2a and 2b in chloroform at 60° C, gives hexamethyldisiloxane 3 and unsymmetrical disulphides 4 (Equation 1).

$$\underset{\mathbf{1}}{R-\overset{\overset{O}{\|}}{S}-S-R} + \underset{\mathbf{2}}{2\ R^1-S-SiMe_3} \longrightarrow \underset{\mathbf{4}}{2\ R-S-S-R^1} + \underset{\mathbf{3}}{Me_3Si-O-SiMe_3} \qquad (1)$$

$R = Me, Ph, p\text{-}Tol;\ R^1 = Me, Ph$

The thiosulphonates **5** also react with **2** to give **4** and the silyl esters of the sulphinic acids **6** (Equation 2).



$$\underset{\mathbf{5}}{R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-R} + \underset{\mathbf{2}}{R^1-S-SiMe_3} \longrightarrow \underset{\mathbf{4}}{R-S-S-R^1} + \underset{\mathbf{6}}{R-\overset{\overset{O}{\|}}{S}-OSiMe_3} \qquad (2)$$

R = Me, Et, p–Tol; R^1 = Me, Ph

Yields and conditions for the reaction described in the equations are reported in the Table[3].

Table. Reactions of thiosulphinates 1 and thiosulphonates 5 with silylsulphides 2. [a]

Reagent	Silylsulphide	Time (h)	Products (Yields %)		b.p./mmHg °C	Lit. b.p./mmHg °C
MeS(O)SMe **1a**	Ph–S–SiMe$_3$ **2b**	2[b]	MeSSPh **4a**	(90)	86/0.5 mmHg	83–84/1[4]
PhS(O)SPh **1b**	Me–S–SiMe$_3$ **2a**	48	MeSSPh **4a**	(85)[c]	86/0.5 mmHg	83–84/1[4]
p–TolS(O)STol–p **1c**	Me–S–SiMe$_3$ **2a**	113	p–TolSSMe **4b**	(75)	see ref. 7	not given[4]
MeSO$_2$SMe **5a**	Ph–S–SiMe$_3$ **2b**	0.25	MeSSPh **4a**	(73)	86/0.5 mmHg	83–84/1[4]
			MeS(O)OSiMe$_3$ **6a**	(54)	60/0.5 mmHg	35/0.1[5]
EtSO$_2$SEt **5b**	Ph–S–SiMe$_3$ **2b**	0.25	EtSSPh **4c**	(78)	94/0.7 mmHg	123/14[6]
			EtS(O)OSiMe$_3$ **6b**	(52)	46/0.7 mmHg	–[8]
p–TolSO$_2$STol–p **5c**	Me–S–SiMe$_3$ **2a**	36	p–TolSSMe **4b**	(89)	see ref. 7	not given[4]
			p–TolS(O)OSiMe$_3$ **6c**	(71)[d]	–	–

[a] In CHCl$_3$ at 60 °C

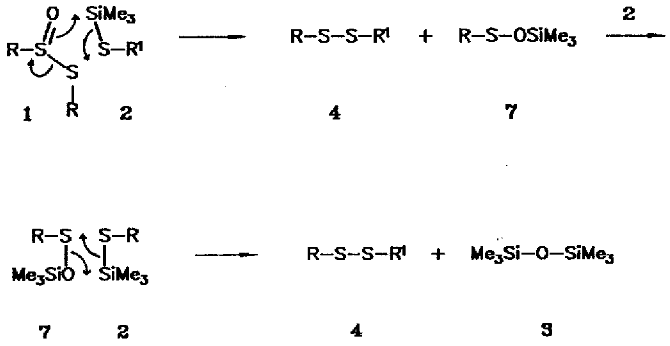
[b] At room temperature

[c] Yield based upon 1b consumed; 1b was recovered in 35% yield

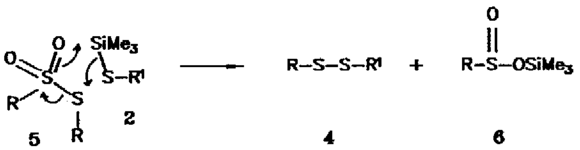
[d] Isolated as sulphinic acid after hydrolysis

The mechanisms proposed for the two reactions are shown in Schemes 1 and 2. Similar pathways have been proposed for the reaction of **1** and **5** with bis(trimethylsilyl)sulphide.[1] As pointed out in the preceding paper either ionic or concerted pathway may be involved;[1] however the latter seems more likely because of the favored five membered transition state and because of the neutral nature of the silylated sulphides.

Scheme 1



Scheme 2



While the mechanism described in Scheme 2 is straightforward, the one proposed for the reaction of thiosulphinates **1** with **2** deserves a few comments. The unsymmetrical disulphide **4** and the silyl ester of the sulphenic acid **7** are suggested to be formed in the first step. In principle, they may react to give randomization of **4**, *via* thiolation of the disulphide.[9] We did not observe this reaction. This might indicate that the reaction rate of **7** with **2** is much faster than that with **4**. This is not unexpected in view of the higher nucleophilic character of the sulphide sulphur with respect to the disulphide sulphur.

It should be noted that, due to the much easier handling of thiosulphonates with respect to thiosulphinates, reaction of Equation 2 seems in our opinion the method of choice for the synthesis of unsymmetrical disulphides.[10] Moreover this reaction gives as "by products" the silyl esters of sulphinic acids **6**[12] which might be the valuable reaction products.

In conclusion, we have shown that silylsulphides are very versatile reagents in organosulphur chemistry. Under neutral and mild conditions they give trisulphides[1] or unsymmetrical disulphides by reaction with thiosulphinates or thiosulphonates. The silylsulphides **2** always behave as reducing agents towards the S = O functionality. This behaviour has been already reported for sulphoxides, which are reduced to sulphides by bis(trimethylsilyl)sulphide.[13,14]

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References and notes

1. G. Capozzi, A. Capperucci, A. Degl'Innocenti, R. Del Duce and S. Menichetti, preceding paper.

2. For a recent review see: K. D. Gundermann and K. Humke in 'Houben-Weyl. Methoden der organischen Chemie' Band E11. G. Thieme Verlag, Stuttgart, 1985, p.129 and references cited therein.

3. All compounds were identified by NMR, GC-MS and comparison with the literature reported physical properties.

4. D. N. Harpp and R. A. Smith, *J. Am. Chem. Soc.*, 1982, **104**, 6045.

5. E. Lindner and K. Schardt, *J. Organomet. Chem.*, 1974, **81**, 145.

6. H. Lecher and M. Wittwer, *Chem. Ber.*, 1922, **55**, 1474.

7. Bulb to bulb distillation at 0.5 mmHg, oil bath at 110 °C. ^{1}H NMR in $CDCl_3$ (300 MHz): δ = 2.357 (s, 3H); 2.450 (s, 3H); 7.16 (A part of a AA'XX' system, apparent d, 2H); 7.44 (X part of a AA'XX'system, apparent d, 2H).

8. ^{1}H NMR in $CDCl_3$ (300 MHz): δ = 0.330 (s, 9H), 1.288 (t, 3H, J = 7.6Hz), 2.84 (q, 2H, J = 7.6Hz). MS, m/e (relative intensity %) 166 (M^+, 7.6), 151 (12), 137 (16), 73 (100).

9. G. Capozzi and G. Modena in 'Organic Sulphur Chemistry. Theoretical and Experimental Advances', F. Bernardi, I. G. Csizmadia and A. Mangini Eds:, Elsevier, Amsterdam, 1985, p.246.

10. It has been shown that **2** reacts with sulphenyl chlorides to give unsymmetrical disulphide.[11] However, the much higher stability of thiosulphonates with respect to sulphenyl chlorides makes our procedure a valuable alternative.

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12. These compounds have been previously prepared from silver sulphinates and trimethylsilyl chloride.[5]

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