On the Synthesis of Sulfoxonium Ylides: New Aspects of the Chemistry of 1,3-Dithietane 1,1,3,3-Tetraoxide and 1,3,5-Trithiane 1,1,3,3,5,5-Hexaoxide

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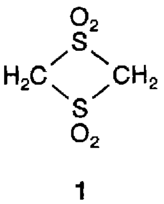
Sulfoxonium ylides **3a–h** were synthesized by silylation of the cyclic methylene disulfones 1,3-dithietane 1,1,3,3-tetraoxide (**1**) and 1,3,5-trithiane 1,1,3,3,5,5-hexaoxide (**4**) with the silylating agents silyl nonafluorobutanesulfonates. The structure and constitution of the ylides were established with ^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR spectroscopy, mass spectrometry, and elemental analysis. On the route to the sulfoxonium ylides a new class of unsaturated disulfenes **7**, **8**, **12**, **13** of **1** and **4** were synthesized via Knoevenagel and substitution reactions. Dianions of newly formed alkyl disulfenes **16a**, **b**, **e**, **f**, and the trianion **17** were prepared and characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy and compared with the results of the ylides.

Alkyl- and silyl-substituted dithiethane 1,1,3,3-tetraoxide (disulfenes) have so far been synthesized mainly with the intention of obtaining (amine-stabilized) sulfenes[1,2]. In these reactions it was observed that during the fourfold silylation of disulfene **1** one of the trimethylsilyl groups[3] and even two of the triethylsilyl groups[4] are attached to the oxygen atoms of the sulfonyl groups, the question whether the C–S bond is a double bond or an ylidic structure being left open. A similar problem arises with the dianions **16**[5] from which we have likewise so far not obtained crystals suitable for an X-ray structural analysis. In this paper we report on our attempts to obtain a further insight into the structure of the disulfenes by a broader variation of the substituents, especially those of structure **3** with heteroatoms or double bonds exerting a favorable effect as well as by a variation of the corresponding cation **16**. Moreover, we describe some analogous reactions of the trimer corresponding to **1**, the 1,3,5-trithiane 1,1,3,3,5,5-hexaoxide **4**, its substitution products and trianion.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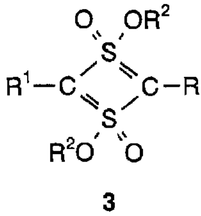
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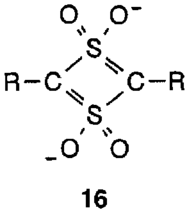
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Stabilization of Sulfoxonium Ylides by Heteroatoms

A few recent publications deal with the preparation of sulfoxonium ylides. Thus, $(FSO_2)_3CH$ is supposed to form the tautomeric species $(FSO_2)_2C{=}S(O)(F)OH$[6] and melting of an open-chain methylene disulfone with diazo compounds was reported to afford a compound containing a phenyl group at the oxygen atom of the sulfonyl group[7]. In addition to the above-mentioned results of the silylation of disulfene **1**[3,4] (preparation as described in refs.[3,8,9]) especially sterical effects of substituents allowing an *O*-silylation and hence stabilization of carbanions were of interest. The square-planar **1**[10,11] is very sensitive to bases[5,12] and exhibits no keto-enol tautomerism in analogy to aldehydes and ketones[13] which allows reactions to be carried out in acidic medium. Substitution reactions of **1** require very strongly alkylating and silylating agents[14,15] available as nonafluorobutanesulfonic acid esters (nonaflates)[3,5,16]. Due to their stronger electrophilic properties they are superior to triflates concerning yields, work-up of the reaction mixture, and their favorable price. The silyl esters $C_4F_9{-}SO_2{-}OR$ (R = $SiMe_3$[3,17], $SiEt_3$[16], $SiMe_2t$Bu[18], $Si i Pr_3$[16], $Si n Bu_3$[16], $SiMe_2Ph$[16,19], $SiPh_3$[16,19]) with increasing sterical hindrance were prepared by reaction of the free acid with alkylchlorosilanes or tetraalkyl/arylsilanes.

Thus, a series of tetrasubstituted compounds **3a–h** were prepared by a two-step synthesis via 2,4-disubstituted disulfenes **2a–h**[3,4]. In contrast to **1** bearing four Me_3Si groups in which only one of the silyl groups migrates to the oxygen atom of the sulfonyl group the NMR spectra of **3a–h** all confirm the symmetrical structure of a 1,3-dioxo-1-λ^6,3λ^6-dithiete which we already detected with **1** bearing four Et_3Si substituents[4]. The solubility in conventional solvents such as THF or diethyl ether increases with increasing size of the substituents. However, since these solvents cannot always be completely separated, **3b**, **3d**, and **3h** were obtained as oils which could only be studied NMR spectroscopically. The other compounds are white powders which partly decompose even under argon. Compound **3g** bearing four *t*-$BuMe_2Si$ groups could be prepared in high yield (82%) which may be attributed to its exceptional stability

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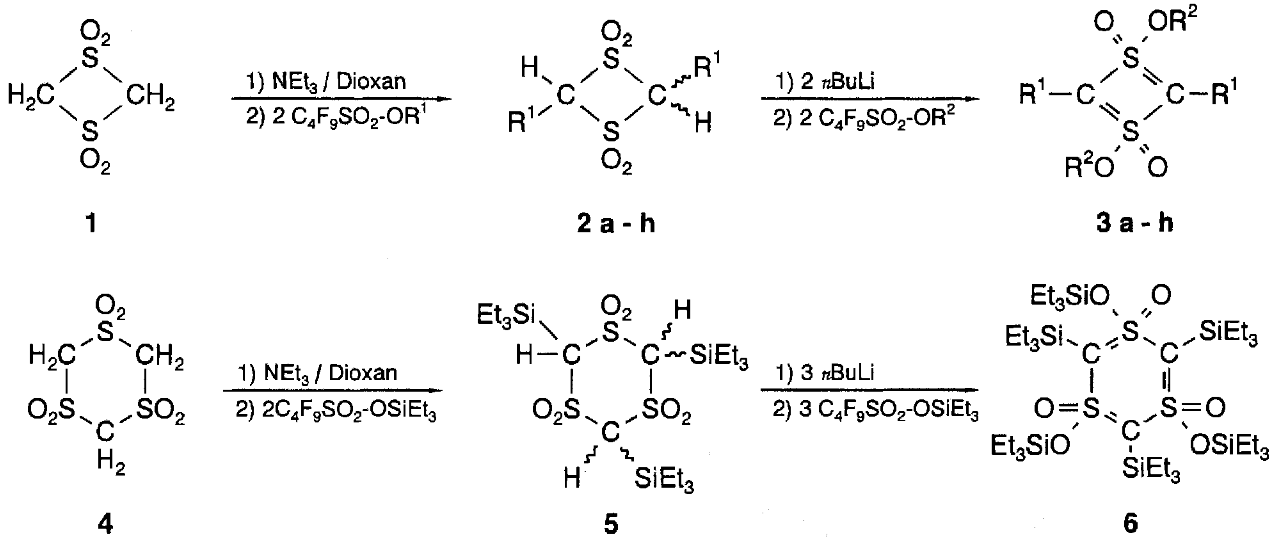


1 **2a-h** **3a-h** **4** **5** **6**

	a	b	c	d	e	f	g	h
R^1	$SiEt_3$	$SiEt_3$	Si*n*Bu_3	Si*n*Bu_3	Si*t*$BuMe_2$	Si*t*$BuMe_2$	Si*t*$BuMe_2$	$SiMe_2Ph$
R^2	Si*i*Pr_3	Si*t*$BuMe_2$	Si*i*Pr_3	Si*n*Bu_3	$SiMe_3$	Si*i*Pr_3	Si*t*$BuMe_2$	$SiMe_2Ph$

caused by sterical hindrance in this series. The constitution of **3g** was established by mass spectrometry and elementary analysis, its ylidic structure by NMR spectroscopy. Whereas signals of non-reacted ring protons are not observed in the ^{1}H-NMR spectrum, splitting of the signals of the methyl groups at silicon both for the substituents at the ring and oxygen atom are recognized. The ^{29}Si-NMR spectrum exhibits at $\delta = -4.9$ and 29.8 the groups at the ring and the oxygen, respectively. All signals in the ^{13}C-NMR spectrum are split in accordance with the two C- and O-substituted groups. Only the signal of the ring atoms at $\delta = 83.0$ points to a negative charge and thus to an ylidic character of the bond while an sp^2 hybridization of the ring carbon atoms is excluded. Although several techniques had been applied **3g** crystallized exclusively as a cotton-like substance. Also the introduction of phenyl rings into **3h** did not afford crystals suitable for an X-ray structural analysis.

After we had previously not succeeded in realizing the corresponding introduction of the Me_3Si groups[20] the trisubstituted **5** could finally be prepared from **4** as the first silylated *s*-trithiane hexaoxide[21,22] and also characterized by elementary analysis. Further metalation of **5** with *n*-butyllithium and subsequent reaction with $C_4F_9-SO_2OSiEt_3$ afforded a viscous oil prone to decompose the spectra of which suggest the existence of **6**. In the ^{1}H-NMR spectrum ring protons are no longer observed while the ^{29}Si-NMR spectrum exhibits a signal at $\delta = 29.5$, pointing to an *O*-silylation, and the ^{13}C-NMR spectrum a signal at $\delta = 76.5$ pointing to the expected ylide.

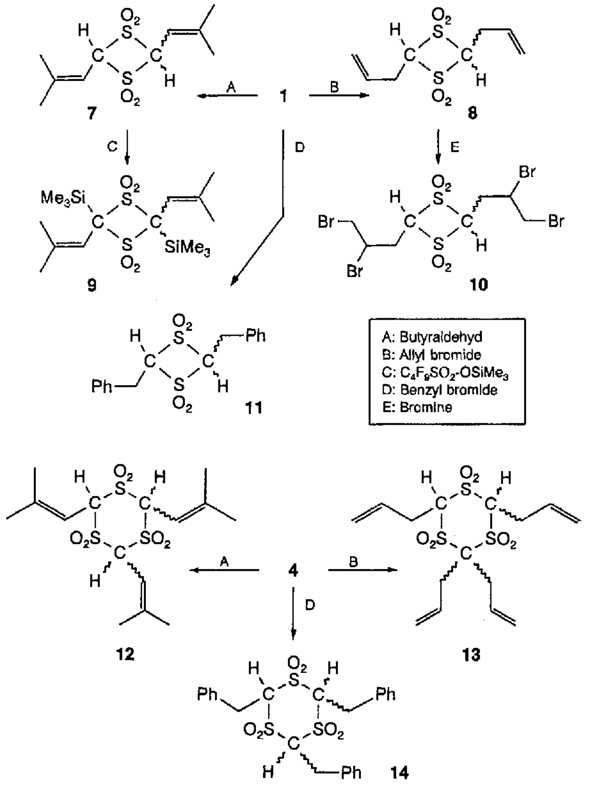
Although an X-ray structural analysis either of **3a**–**h** or **6** could not yet be performed the ylidic structure could be proven NMR spectroscopically by using the exceptionally stable **3g** as an example.

Disulfenes with Unsaturated Substituents

A stabilization of the carbanion on the ring carbon atoms and thus sulfoxonium ylides might be achieved by delocalization of the charge over a (possibly conjugated) π electron system[23]. Utilizing the experiences made in the Knoevenagel reaction of acyclic methylene disulfones[24,25], we treated **1** with isobutyraldehyde in the presence of piperidinium acetate as catalyst in benzene with azeotropic removal of the formed water and obtained **7** bearing unsaturated substituents. To our knowledge this is the first classical reaction of compounds like **1** bearing an acidic hydrogen atom at the carbon atom.

This reaction could also be applied to **4** with the formation of **12**, but not to reactions with other aldehydes (acet-, propione-, and benzaldehyde). Deprotonation of **7** with butyllithium in THF and subsequent reaction with $C_4F_9-SO_2-OSiMe_3$ did not yield a sulfoxonium ylide but **9**, which is a product silylated in 2,4-positions. Sterically more demanding silyl groups could not be introduced and also silylation of **12** failed.

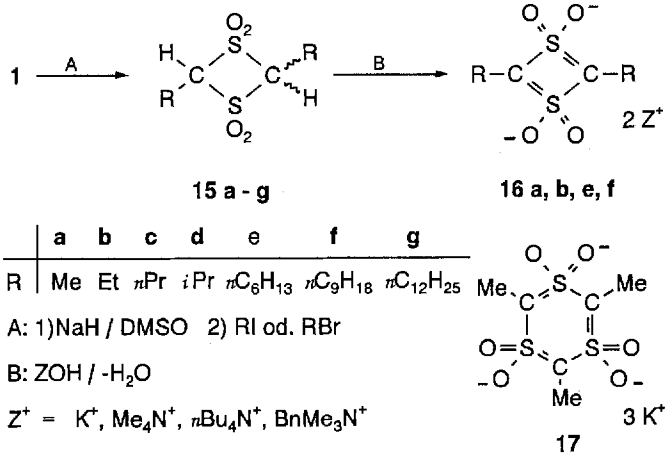
However, **7** displays unusual properties. Its double bonds are resistant to all typical reactions such as bromination, dihydroxylation with $KMnO_4$, ozonolysis, and epoxidation. The same is true for **12**. In order to find out whether the low reactivity might be caused by the disulfene ring, **1** was treated with NaH and allyl bromide in DMSO (analogously as described in ref.[4]) to afford **8** in which the double bond is distant from the ring by a CH_2 group. The same reaction with **4** furnished a mixture of different substitution products from which **13** could be isolated by column chromatography. Since both **8** and **13** undergo the typical olefin reactions, e.g. bromination in ethanol affording **10**, it could in-



directly be shown that the methylenesulfone rings of **7** and **12** reduce the electron density of the adjacent double bond and hence the reactivity toward electrophiles. The *O*-silylation and stabilization of ylides could not be achieved in this way which also applies to **11** and **14** formed by the reaction of **1** and **4**, respectively, with benzyl bromide.

Dianions of Alkylated Disulfenes

During the past decade sulfones have gained increasing importance in preparative chemistry[26]. Therefore, data on the structure of α-carbanions of sulfones, important intermediates of the reaction, are of particular interest[27,28]. Compared with these acyclic compounds the dianion **16a** of the conformatively blocked methylene disulfone **15a** seems to display exceptional structural properties[5]. Also in this case it had to be clarified whether **16a** is an ylidic system or possesses an enol-like structure. The ^{13}C-NMR spectrum of the dipotassium salt **16a** exhibits a signal at $\delta = 179.45$ of the ring carbon atoms indicating sp^2 hybridization. In contrast, the CH_3 groups give rise to ^{1}H-NMR signals at $\delta = 1.19$ and 1.46 suggesting *cis*/*trans* isomerism with retention of sp^3 hybridization and excluding a planar ring. Since suitable crystals were not available, an X-ray structural analysis could not be performed although we originally used pure *trans*-**15a**[5]. In order to affect solubility and thus to improve recrystallization of the dianions to be prepared different 2,4-dialkylated disulfenes **15a**–**g** were synthesized and characterized. They were obtained as colorless crystalline *cis*/*trans* mixtures with distinct melting points. Besides further deprotonation of **15a** also **15b**, **15e**, and **15f** were treated with KOH in methanol at 10°C, the solvent was evaporated and **16a**, **b**, **e**, **f** were obtained in quantitative yield. Moreover, **15a**, and **15b** were deprotonated by treatment with the bases Me_4NOH, $BzlMe_3NOH$, and Bu_4NOH and the NMR spectra of the corresponding salts were recorded in [D$_6$]DMSO. ^{13}C-NMR signals of the quaternary ring carbon atoms could however not always be obtained. However, the found values confirm our earlier results[5]. While for the acyclic compounds $PhCHLiSO_2{-}CH_3$ and $PhCHLiSO_2{-}t\mathrm{Bu}$ ^{13}C-NMR signals at $\delta = 59.8$ and 51.5, respectively, attributed to the degree of hybridization between sp^2 and sp^3, were reported[29] we observed for the potassium salt of **16a** as well as for the $BzlMe_3N^+$ salts of **16a** and **16b** ^{13}C-NMR signals at $\delta = 179.5$, 185.8, and 158.5, respectively, indicating sp^2 hybridization. The signal for the ring carbon atoms of the tripotassium salt **17** prepared from the 2,4,6-trimethyl-1,3,5-trithiane 1,1,3,3,5,5-hexaoxide[20] appears at $\delta = 184.3$. The ^{1}H-NMR spectra are inconsistent with a planar ring system since the original *cis*/*trans* isomerism of **15** and **16** seems to be retained. These contradictory data can only be reconciled with a strongly twisted ring. The failure to perform an X-ray structural analysis could thus also be accounted for since such a molecule is prone to undergo ring opening.



15 a - g

16 a, b, e, f

17

	a	b	c	d	e	f	g
R	Me	Et	*n*Pr	*i*Pr	*n*C_6H_{13}	*n*C_9H_{18}	*n*$C_{12}H_{25}$

A: 1) NaH / DMSO 2) RI od. RBr

B: ZOH / $-H_2O$

Z^+ = K^+, Me_4N^+, *n*Bu_4N^+, $BnMe_3N^+$

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Experimental

If not stated otherwise, all experiments were carried out under argon with the exclusion of moisture and air. Solvents were dried by means of conventional methods. Nonafluorobutanesulfonates and disulfene **1** as well as 1,3,5-trithiane 1,1,3,3,5,5-hexaoxide **5** were prepared according to literature procedures[4,16,22]. A glove box filled with dried argon was used for the preparation of solid products.

IR: IFS 88 Bruker. – NMR (internal standard: TMS for ^{1}H, ^{13}C and ^{29}Si, CCl_3F for ^{19}F): Joel FX-90 Q. – MS: VG 7070. – Elemental analysis: Mikroanalytische Abteilung der Chemischen Institute der Universität Heidelberg. – Melting points: uncorrected.

Dimethylphenylsilyl and Triphenylsilyl Nonafluorobutanesulfonates: Both esters were prepared by reaction of silver nonafluorobutanesulfonate with dimethylphenyl- and triphenylchlorosilane[16], respectively, requiring however several days. On the other hand, dimethyldiphenylsilane and tetraphenylsilane easily accessible via Grignard syntheses react with $C_4F_9SO_2OH$ within several hours with cleavage of a phenyl group as benzene.

A heat-dried 100-ml flask was charged under argon with 13.07 g (61.6 mmol) of dimethyldiphenylsilane to which 18.47 g (61.6 mmol) of acid was slowly added with ice cooling. The resulting ruby-colored solution was stirred for 30 min, the formed benzene was subsequently evaporated under high vacuum and the residue subjected to fractional distillation to afford 24.2 g of $C_4F_9SO_2{-}SiMe_2Ph$ (90.5%); b.p. 74–77 °C/10^{-3} Torr.

To a suspension of 11.58 g (34.3 mmol) of tetraphenylsilane in 50 ml of absolute benzene was slowly added with stirring 10.33 g (34.3 mmol) of $C_4F_9SO_2OH$, the suspension was then heated at 70 °C for 1 h and further stirred at room temp. for 5 h. After fractional distillation 9.6 g (50%) of $C_4F_9SO_2{-}OSiPh_3$ was obtained, b.p. 170 °C/10^{-3} Torr. For physical data see ref.[16].

General Method for the Preparation of Sulfoxonium Ylides (**3a–h**): In a 100-ml Schlenk flask equipped with a septum 2.79 mmol of silylated disulfene (**2a–h**) was dissolved in 20 ml of anhydrous THF. The solution was treated at −40 °C with 5.58 mmol of a 1.6 M *n*-BuLi solution in *n*-hexane (bismetalation) during 15 min and the mixture was subsequently stirred at −40 °C for 60 min. After the addition of 5.58 mmol of trialkylsilyl nonafluorobutanesulfonate within 30 min the mixture was further stirred at this temp. for 30 min. It was subsequently allowed to warm to room temp. during 60 min. The solvent was then evaporated under high vacuum. The remaining solid was extracted twice with 10 ml of cold anhydrous *n*-hexane each. The combined extracts were separated from the remaining lithium nonaflate by filtration through a G4 reverse frit. After evaporation of the hexane and drying of the product under high vacuum either a white powder or a yellow oil was obtained. Both forms of sulfoxonium ylides easily decompose.

1,3-Bis(triisopropylsiloxy)-2,4-bis(triethylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3a**): White powder easily decomposing even under argon. – ^1H NMR ($CDCl_3$): δ = 0.98 [m, 30H, 2 $CSi(CH_2CH_3)_3$], 1.16 [m, 42H, 2 $OSi(CH(CH_3)_2)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 4.6 [s, $Si(CH_2CH_3)_3$], 7.7 [s, $Si(CH_2CH_3)_3$], 13.3 [s, $Si(CH(CH_3)_2)$], 18.1 $Si(CH(CH_3)_2)$], 84.6 (s, ring C atoms). – ^{29}Si NMR ($CDCl_3$): δ = −4.9 (s, CSi), 28.0 (s, OSi). – MS (70 eV), *m/z* (%): 696 (79.8) [M^+], 87 (100.0).

1,3-Bis(tert-butyldimethylsiloxy)-2,4-bis(triethylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3b**): Yellow oil. – ^1H NMR ($CDCl_3$): δ = 0.37 [m, 12H, 2 $OSi(CH_3)_2$], 0.95 [m, 30H, 2 $CSi(CH_2CH_3)_3$], 1.00 [s, 18H, 2 $OSi(C(CH_3)_3)$]. – ^{13}C NMR ($CDCl_3$): δ = −3.6 [s, $Si(CH_3)_2$], 4.5 [s, $Si(CH_2CH_3)_3$], 7.5 [s, $Si(CH_2CH_3)_3$], 18.2 [s, $Si(C(CH_3)_2)$], 25.5 [s, $Si(C(CH_3)_2)$], 82.2 (s, ring C atoms). – ^{29}Si NMR ($CDCl_3$): δ = −0.6 (s, CSi), 34.1 (s, OSi).

1,3-Bis(triisopropylsiloxy)-2,4-bis(tri-n-butylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3c**): Yellow solid, very sensitive to hydrolysis. Yield 80%. – IR (KBr): $\tilde{\nu}$ = 2955.4 cm^{-1} (vs), 2924.5 (vs), 2870.5 (m), 1464.7 (m), 1212.1 (m), 1077.1 (m), 889.0 (s), 855.3 (s). – ^1H NMR ($CDCl_3$): δ = 0.84 [t, 18H, 2 $CSi(CH_2CH_2CH_2CH_3)_3$], 1.15 [m, 42H, 2 $OSi(CH)(CH_3)_2)_3$], 1.24 [m, 48H, 2 $CSi(CH_2CH_2CH_2CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 13.4 [s, $Si(CH(CH_3)_2)_3$], 14.0 [s, $Si(CH_2CH_2CH_2CH_3)_3$], 14.6 [s, $Si(CH_2CH_2CH_2CH_3)_3$], 18.1 [s, $Si(CH(CH_3)_2)_3$], 26.2 [s, $Si(CH_2CH_2CH_2CH_3)_3$], 27.0 [s, $Si(CH_2CH_2CH_2CH_3)_3$], 84.9 (s, ring C atoms). – ^{29}Si NMR ($CDCl_3$): δ = −9.3 (s, CSi), 27.3 (s, OSi). – MS (70 eV), *m/z* (%): 708 (0.3) [M^+ − 157 ($Si(C_3H_7)_3$)], 75 (100.0).

1,3-Bis(tri-n-butylsiloxy)-2,4-bis(tri-n-butylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3d**): Yellow easily decomposing oil. – ^1H NMR ($CDCl_3$): δ = 0.88 [m, 54H, 2 $CSi(C_4H_9)_3$], 1.32 [m, 54H, 2 $OSi(C_4H_9)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 12.6, 14.0, 14.6, 16.3, 25.3, 25.5, 25.7, 25.9, 26.5, 26.6, 26.9, 27.1 (each s), 68.3 (s, ring, C atoms). – ^{29}Si NMR ($CDCl_3$): δ = −9.6 (CSi), 27.4 (s, OSi).

1,3-Bis(trimethylsiloxy)-2,4-bis(tert-butyldimethylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3e**): White thread-like crystals. Yield 76.6%. – ^1H NMR ($CDCl_3$): δ = 0.40 [s, 12H, 2 $Si(CH_3)_2$], 0.43 [s, 18H, 2 $Si(CH_3)_3$], 0.99 [s, 18H, 2 $Si(C(CH_3)_3)$]. – ^{13}C NMR ($CDCl_3$): δ = −6.4 [s, $CSi(CH_3)_3$], 2.2 (s, $OSi(CH_3)_2$], 16.8 [s, $CSiC(CH)_3)_3$], 26.4 [s, $CSiC(CH_3)_3$], 99.9 (s, ring C atoms). – MS (70 eV), *m/z* (%): 528 (0.1) [M^+], 73 (100.0).

1,3-Bis(triisopropylsiloxy)-2,4-bis(tert-butyldimethylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3f**): White thread-like crystals. Yield 56.6%, m.p. 82 °C (dec.). – ^1H NMR ($CDCl_3$): δ = 0.16 [s, 12H, 2 $Si(CH_3)_2$], 0.99 [s, 18H, 2 $Si(C(CH_3)_3$], 1.19 [s, 42H, 2 $Si(CH(CH_3)_2)$]. – ^{13}C NMR ($CDCl_3$): δ = −4.19 [s, $Si(CH_3)_2$], 13.44 [s, $OSiCH(CH_3)_2$], 18.05 [s, $CSiC(CH_3)_2$], 18.51 [s, $OSiCH(CH_3)_2$], 26.96 [s, $CSiCH(CH_3)_2$], 85.75 (s, ring C atoms). – ^{29}Si NMR ($CDCl_3$): δ = −5.21 (s, CSi), 27.91 (s, OSi). – MS (70 eV), *m/z* (%): 696 (100.0) [M^+].

1,3-Bis(tert-butyldimethylsiloxy)-2,4-bis(tert-butyldimethylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3g**): White crystals, relatively stable to hydrolysis. Yield 82.0%, m.p. 89 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2932.3 cm^{-1} (m), 2915.9 (s), 1472.4 (w), 1329.7 (vs), 1256.4 (m), 1155.2 (vs), 1092.5 (m), 849.5 (m), 821.5 (m). – ^1H NMR ($CDCl_3$): δ = 0.16 [s, 12H, 2 $CSi(CH_3)_2$], 0.40 [s, 12H, 2 $OSi(CH_3)_2$], 0.96 [s, 18H, 2 $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = −4.5 [s, $CSi(CH_3)_2$], −3.3 [s, $OSi(CH_3)_3$], 18.2 [s, $CSiC(CH_3)_3$], 18.4 [s, $OSiC(CH_3)_3$], 25.5 [s, $CSiC(CH_3)_3$], 26.8 [s, $OSiC(CH_3)_3$], 82.9 (s, ring C atoms). – ^{29}Si NMR ($CDCl_3$): δ = −4.9 (s, CSi), 29.8 (s, OSi). – MS (70 eV), *m/z* (%): 612 (6.3) [M^+], 73 (100.0). – $C_{26}H_{60}O_4S_2Si_4$ (613.23): calcd. C 50.92, H 9.86, S 10.46; found C 50.86, H 10.07, S 10.56.

1,3-Bis(dimethylphenylsiloxy)-2,4-bis(dimethylphenylsilyl)-1,3-dioxo-1λ^6*,3*λ^6*-dithiete* (**3h**): Yellow oil, easily decomposing. – ^1H NMR ($CDCl_3$): δ = 0.69 [s, 12H, 2 $CSi(CH_3)_2$], 0.98 [s, 12H, 2 $OSi(CH_3)_2$], 7.40–7.50 (m, 20H, 4 phenyl). – ^{13}C NMR ($CDCl_3$): δ = 1.0, 1.2, 14.6, 16.3 (each s), 94.2 (s, ring C atoms), 127.9, 128.1, 129.4, 130.4, 130.7, 131.3, 133.2, 134.4, 135.7, 137.5 (each s, phenyl C atoms). – ^{29}Si NMR ($CDCl_3$): δ = −9.6 (s, CSi), 27.4 (s, OSi).

2,4,6-Tris(triethylsilyl)-1,3,5-trithiane 1,1,3,3,5,5-Hexaoxide (**5**): In a 250-ml two-neck flask equipped with reflux condenser and septum 3.00 g (12.8 mmol) of **4** was suspended in 90 ml of abs. dioxane. Then 6.00 g (57.7 mmol) of NEt_3 was added in one portion to the suspension which was stirred for 5 min. Subsequently, 23.9 g (57.7 mmol) of triethylsilyl nonafluorobutanesulfonate was added dropwise during 30 min and the mixture was stirred at room temp. for 1 h. Stirring was continued at 70 °C for a further hour. During this period **4** gradually dissolved. The resulting brown, clear reaction solution was transferred to a 500-ml Schlenk flask with the exclusion of air and the dioxane was evaporated under high vacuum. The dark brown residue was heated at reflux in ca. 250 ml of petroleum ether (60–70 °C) for 30 min and the hot light brown solution was then decanted from insoluble triethylammonium nonafluorobutanesulfonate with the exclusion of air and the product was crystallized at −35 °C. The obtained light brown crystals were recrystallized from 250 ml of petroleum ether (60–70 °C). Yield 4.75 g (64.4%), m.p. >250 °C. – IR (KBr): $\tilde{\nu}$ = 2957.3 cm^{-1}

(vs), 2914.9 (vs), 2880.2 (vs), 1336.4 (vs), 1168.7 (s), 1130.1 (s), 1119.5 (s), 833.1 (s). – ^{1}H NMR ($CDCl_3$): δ = 1.01 [m, 45H, $Si(CH_2CH_3)_3$], 4.71, 5.03 (each s, 3H, HC). – ^{13}C NMR ($CDCl_3$): δ = 5.8 [s, $Si(CH_2CH_3)_3$], 6.4 [s, $Si(CH_2CH_3)_3$], 68.0 (s, ring C atoms). – ^{29}Si NMR ($CDCl_3$): δ = 13.30 (s). – MS (70 eV), *m/z* (%): 547 (100.0) [M^+ – 29 (C_2H_5)]. – $C_{21}H_{48}O_6S_3Si_3$ (577.07): calcd. C 43.71, H 8.39, S 16.67; found C 43.46, H 8.33, S 16.88.

1,3,5-Tris(triethylsiloxy)-2,4,6-tris(triethylsilyl)-1,3,5-trioxo-1λ⁶,3λ⁶,5λ⁶-trithiete (**6**): In a 100-ml Schlenk flask equipped with a septum 1.00 g (1.7 mmol) of **5** was dissolved in 40 ml of anhydrous DME. Metalation of **5** was performed by adding to the resulting solution at –30°C during 15 min 3.3 ml (5.3 mmol) of a 1.6 M *n*-BuLi solution in hexane and the mixture was subsequently stirred at this temperature for 60 min. After the addition of 2.19 g (5.3 mmol) of triethylsilyl nonafluorobutanesulfonate within 30 min a clear yellow solution was obtained which was stirred for further 30 min and then allowed to warm to room temp. within 60 min. After evaporation of the solvent under high vacuum a white solid besides a yellow oil was obtained. The viscous oil was separated from the solid by twofold extraction with anhydrous *n*-hexane. Evaporation of the *n*-hexane yielded **6** as a clear orange and easily decomposable oil. The yield – as with all oily ylides – could not be determined since the solvent could not be completely separated. – ^{1}H NMR ($CDCl_3$): δ = 0.94 [m, 45H, 3 $CSi(CH_2CH_3)_3$], 1.01 [m, 45H, 3 $OSi(CH_2CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 4.3 [s, $CSi(CH_2CH_3)_3$], 4.7 [s, $OSi(CH_2CH_3)_3$], 7.0 [s, $OSi(CH_2CH_3)_3$], 7.3 (s, $OSi(CH_2CH_3)_3$], 76.5 (s, ring C atoms). – ^{29}Si NMR ($CDCl_3$): δ = 3.6 (s, CSi), 29.5 (s, OSi).

2,4-Bis(2-methylprop-1-en-1-yl)-1,3-dithietane 1,1,3,3-Tetraoxide (**7**): In a 500-ml single-neck flask 10.0 g (63.3 mmol) of **1**, 63.8 g (886 mmol) of isobutyraldehyde and 0.63 g (4.3 mmol) of piperidinium acetate were heated at reflux in 250 ml of benzene in a water trap until no more water separated (ca. 24 h). During this period the disulfene dissolved. The benzene was subsequently evaporated under high vacuum and the remaining yellow malodorous residue was twice recrystallized from ethanol to afford white crystals. Yield 9.1 g (54.5%), m.p. 150°C. – IR (KBr): ṽ = 2969.9 cm^{-1} (m), 1652.7 (m), 1366.3 (s), 1334.5 (vs), 1156.1 (vs), 1081.9 (m), 832.1 (w), 521.7 (m). – ^{1}H NMR ([D_6]DMSO): δ = 1.80 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.91 (s, 6H, 2 CH_3), 5.37 (d, 1H, CH=C, $^3J_{H,H}$ = 9.7 Hz), 5.56 (d, 1H, CH=C, $^3J_{H,H}$ = 9.3 Hz), 7.26 (d, 1H, HC, $^3J_{H,H}$ = 9.7 Hz), 7.38 (d, 1H, HC, $^3J_{H,H}$ = 9.3 Hz). – ^{13}C NMR ([D_6]DMSO): δ = 19.9 (s, CH_3), 26.3 (s, CH_3), 97.7 (s, ring C atoms), 99.9 (s, ring C atoms), 106.6, 108.0 (2 s, –CH=), 149.3, 149.5 (2 s, =CCH_3). – MS (70 eV), *m/z* (%): 264 (2.2) [M^+], 136 (100.0). – $C_{10}H_{16}O_4S_2$ (264.37): calcd. C 45.43, H 6.10, S 24.21; found C 45.64, H 6.07, S 24.20.

2,4-Bis(prop-2-en-1-yl)-1,3-dithietane 1,1,3,3-Tetraoxide (**8**): To a suspension of 3.00 g (19.2 mmol) of **1** and 925 mg (38.5 mmol) of NaH in 50 ml of anhydrous DMSO was cautiously added dropwise within 30 min 4.65 g (38.5 mmol) of allyl bromide. In a slightly exothermic reaction a clear brown solution was obtained which was heated at 65°C for 1 h. The reaction mixture was hydrolyzed with 50 g of ice and the formed colorless precipitate was recrystallized from 20 ml of methanol to furnish colorless crystals. Yield 260 mg (5.8%), m.p. 111°C. – IR (KBr): ṽ = 3093.2 cm^{-1} (w), 2953.5 (vs), 1645.0 (m), 1428.0 (m), 1346.1 (vs), 1159.0 (vs), 1079.0 (s), 935.3 (s), 488.9 (s). – ^{1}H NMR ([D_6]DMSO): δ = 2.96 (m, 8H, 4 CH_2), 5.26 (m, 8H, 4 =CH_2, $^3J_{H,H}$ = 7.6 Hz), 5.61–6.05 (2 m, je 2H, 4 –CH=C), 6.52 (t, 2H, 2 HC, $^3J_{H,H}$ = 7.6 Hz, *trans*-**9**), 6.81 (t, 2H, HC, $^3J_{H,H}$ = 7.6 Hz, *cis*-**9**). – ^{13}C NMR ([D_6]DMSO): δ = 27.9 (s, $-CH_2-$), 29.4 (s, $-CH_2-$), 97.0 (s, ring C atoms), 98.3 (s, ring C atoms), 119.2, 119.4 (2 s, =CH_2), 130.2, 130.4 (2 s, =CH_2). – MS (70 eV), *m/z* (%): 236 (1.8) [M^+], 54 (100.0). – $C_8H_{12}O_4S_2$ (236.31): calcd. C 40.66, H 5.12, S 27.14; found C 40.44, H 5.07, S 27.29.

2,4-Bis(2-methylprop-1-en-1-yl)-2,4-bis(trimethylsilyl)-1,3-dithietane 1,1,3,3-Tetraoxide (**9**): In a 100-ml Schlenk flask 1.00 g (3.79 mmol) of **7** was dissolved in 50 ml of anhydrous THF and the solution was cooled to –40°C. To this was added dropwise within 15 min 4.74 ml (7.58 mmol) of a 1.6 M solution of *n*-BuLi in hexane. The mixture was stirred at this temperature for 1 h. Subsequently, 2.82 g (7.58 mmol) of trimethylsilyl nonafluorobutanesulfonate was added dropwise within 30 min and the reaction mixture was further stirred at –40°C for 60 min. During this period the mixture turned bright yellow. It was then allowed to warm to room temp. and the solvent was evaporated under high vacuum. The residue was extracted at room temp. with 10 ml of anhydrous *n*-hexane and the insoluble lithium nonaflate was separated by filtration through a G4 reverse frit. After evaporation of the *n*-hexane under high vacuum a yellow, extremely unstable precipitate was obtained decomposing within several days in the glove box. – ^{1}H NMR ($CDCl_3$): δ = 0.33 [s, 18H, 2 $Si(CH_3)_3$], 1.73 (s, 6H, 2 CH_3), 1.92 (s, 6H, 2 CH_3), 5.53 (s, 2H, 2 –CH=C). – ^{29}Si NMR ($CDCl_3$): δ = 13.99 (s). – MS (70 eV), *m/z* (%): 410 (0.4) [M^+], 73 (100.0).

2,4-Bis(2,3-dibromoprop-1-yl)-1,3-dithietane 1,1,3,3-Tetraoxide (**10**): To a solution of 220 mg (0.93 mmol) of **8** in 20 ml of ethanol was slowly added dropwise 0.30 g (1.87 mmol) of bromine. During this addition a white precipitate formed. After the mixture had been stirred at room temp. for 1 h the precipitate was filtered off and recrystallized from ethanol to afford a white powder. Yield quantitative, m.p. 180°C. – IR (KBr): ṽ = 2943.8 cm^{-1} (m), 1381.8 (s), 1354.8 (vs), 1315.2 (s), 1170.6 (s), 1150.3 (vs), 918.9 (m), 843.7 (m), 689.4 (w), 580.5 (w), 492.7 (w). – ^{1}H NMR ([D_6]DMSO): δ = 3.02 (m, 2H, CH_2), 4.06 (m, 2H, CH_2Br), 4.56 (m, 2H, CHBr), 6.56 (t, 1H, HC), 6.89 (t, 1H, HC). – ^{13}C NMR ([D_6]DMSO): δ = 31.2 (s, CH_2Br), 32.6 (s, CH_2Br), 37.0 (s, CHBr), 48.6 (CH_2), 97.1 (s, ring C atoms), 98.6 (s, ring C atoms). – MS (70 eV), *m/z* (%): 475 (14.7) [M^+ – 79 (Br)], 53 (100.0).

2,4-Dibenzyl-1,3-dithietane 1,1,3,3-Tetraoxide (**11**): To a mixture of 1.00 g (6.41 mmol) of **1** and 308 mg (12.8 mmol) of NaH in 50 ml of anhydrous DMSO was added dropwise within 30 min 2.19 g (12.8 mmol) of benzyl bromide during which time a clear brown solution formed which was stirred at room temp. for 1 h (heating must strictly be avoided). The reaction mixture was hydrolyzed with 50 g of ice and the formed colorless precipitate was filtered off. The product was dissolved in hot ethanol and crystallized at –18°C to afford colorless crystals. Yield 1.30 g (31.7%), m.p. 175°C. – IR (KBr): ṽ = 3063.4 cm^{-1} (m), 3029.6 (m), 2961.2 (s), 1333.5 (vs), 1148.4 (s), 1082.8 (m), 1028.8 (w), 738.6 (m), 702.0 (m), 476.3 (w). – ^{1}H NMR ([D_6]DMSO): δ = 3.55 (d, 4H, 2 CH_2), 6.74–7.10 (2 t, 2H, 2 HC), 7.36 (m, 10H, 2 phenyl). – ^{13}C NMR ([D_6]DMSO): δ = 29.8 (s, CH_2), 31.2 (s, CH_2), 98.4 (s, ring C atoms), 99.9 (s, ring C atoms), 127.4–133.7 (m, phenyl). – MS (70 eV), *m/z* (%): 336 (7.1) [M^+], 91 (100.0). – $C_{16}H_{16}O_4S_2$ (336.43): calcd. C 57.12, H 4.80, S 19.06; found C 56.98, H 4.74, S 18.93.

2,4,6-Tris(2-methylprop-1-en-1-yl)-1,3,5-trithiane 1,1,3,3,5,5-Hexaoxide (**12**): According to the procedure used for the preparation of **7**, 11.7 g (50 mmol) of 1,3,5-trithiane 1,1,3,3,5,5-hexaoxide (**4**) was allowed to react with 75.7 g (1.05 mmol) of isobutyraldehyde and 0.5 g (3.4 mmol) of piperidinium acetate in 250 ml of benzene. The reaction time was 72 h. Yield 4.57 g (23%), m.p. 258 (dec.). – IR (KBr): ṽ = 2939.0 cm^{-1} (m), 1650.8 (m), 1448.3 (m), 1345.1 (vs), 1136.8 (vs), 800.3 (s), 606.5 (vs), 501.4 (m). – ^{1}H NMR ([D$_6$]DMSO): δ = 1.84 (s, 9H, 3 CH_3), 1.96 (s, 9H, 3 CH_3), 5.28 (d, 3H, 3 CH=C, $^{3}J_{H,H}$ = 10.6 Hz), 6.66 (d, 3H, 3 HC, $^{3}J_{H,H}$ = 10.6 Hz). – ^{13}C NMR ([D$_6$]DMSO): δ = 19.3 (s, CH_3), 26.0 (s, CH_3), 78.7 (s, ring C atoms), 99.1 (s, –CH=), 154.5 (s, =CCH_3). – MS (70 eV), *m/z* (%): 332 (5.0) [M$^+$ – 64 (SO_2)], 136 (100.0). – $C_{15}H_{24}O_6S_3$ (396.55): calcd. C 45.43, H 6.10, S 24.21; found C 45.48, H 6.15, S 24.03.

2,2,4,6-Tetrakis(prop-2-en-1-yl)-1,3,5-trithiane 1,1,3,3,5,5-Hexaoxide (**13**): As described for **8** 3.00 g (12.8 mmol) of **4** was allowed to react with 1.23 g (51.2 mmol) of NaH and 6.2 g (51.2 mmol) of allyl bromide. After hydrolysis with ca. 50 g of ice and filtration of the precipitate **13** was isolated by column chromatography [column 30 × 3 cm, eluent ethyl acetate/petroleum ether (60–70 °C), 1:1, silica gel, R_f = 0.48]. The isolated colorless precipitate was recrystallized from ethanol to afford colorless crystals. Yield 260 mg (5.2%), m.p. 141 °C. – IR (KBr): ṽ = 3085.6 cm^{-1} (w), 2946.7 (w), 1642.1 (w), 1429.0 (w), 1352.8 (vs), 1337.4 (s), 1148.4 (m), 1126.2 (m), 931.5 (m), 607.5 (w). – ^{1}H NMR ([D$_6$]DMSO): δ = 3.04 (m, 8H, 4 CH_2), 5.38 (m, 8H, 4 =CH_2), 5.98 (m, 6H, HC, –CH=). – ^{13}C NMR ([D$_6$]DMSO): δ = 23.6, 24.6, 32.4 (each s, –CH_2–), 74.0, 75.8, 86.6, 88.4 (each s, ring C atoms), 119.9, 122.4 (2 s, = CH_2), 128.7, 130.6 (2 s, =CH_2). – MS (70 eV), *m/z* (%): 394 (3.7) [M$^+$], 41 (100.0). – $C_{15}H_{22}O_6S_3$ (394.53): calcd. C 45.67, H 5.62, S 24.38; found C 45.56, H 5.58, S 24.38.

2,4,6-Tribenzyl-1,3,5-trithiane 1,1,3,3,5,5-Hexaoxide (**14**): As described for **11** 1.00 g (4.27 mmol) of **4** was allowed to react with 308 mg (12.8 mmol) of NaH and 2.19 g (12.8 mmol) of benzyl bromide in 30 ml of anhydrous DMSO. After crystallization at –18 °C colorless crystals were obtained. Yield 1.30 g (31.7%), m.p. >250 °C. – IR (KBr): ṽ = 2933.2 cm^{-1} (w), 1437.7 (w), 1361.5 (vs), 1340.3 (s), 1171.6 (s), 1138.8 (s), 792.6 (s), 697.1 (s), 637.4 (w), 486.9 (m). – ^{1}H NMR ([D$_6$]DMSO): δ = 3.55 (d, 6H, 3 CH_2), 6.06 (t, 3H, 3 HC), 7.31 (m, 15H, 3 phenyl). – ^{13}C NMR ([D$_6$]DMSO): δ = 24.1 (s, CH_2), 78.5 (s, ring C atoms), 127.5–135.9 (m, phenyl). – MS (70 eV), *m/z* (%): 504 (0.2) [M$^+$], 91 (100.0). – $C_{24}H_{24}O_6S_3$ (504.65): calcd. C 57.12, H 4.80, S 19.06; found C 56.83, H 4.79, S 19.02.

General Procedure for the Preparation of Long-Chain Disulfenes (**15c, e, f, g**): To a suspension of 3 g (19.2 mmol) of **1** and 925 mg (38.5 mmol) of NaH in 50 ml of anhydrous DMSO was added dropwise within 40 min 38.5 mmol of the corresponding alkyl bromide. In a slightly exothermic reaction a clear, brown solution was formed which was heated at 65 °C for 1 h. The reaction mixture was subsequently poured on 50 g of ice and the obtained yellow viscous substance was extracted with ethyl acetate. The solvent was evaporated from the extract in a rotary evaporator and the residue was taken up in 20 ml of ethanol. The product crystallized at –18 °C as white crystals.

2,4-Di-n-propyl-1,3-dithietane 1,1,3,3-Tetraoxide (**15c**): Yield 1.87 g (40%), m.p. 80 °C. – IR (KBr): ṽ = 2961.2 cm^{-1} (s), 2949.6 (s), 2876.3 (m), 1466.6 (m), 1327.8 (vs), 1166.7 (vs), 1102.1 (vs), 829.2 (m), 682.7 (m), 497.6 (m), 424.3 (m). – ^{1}H NMR ([D$_6$]DMSO): δ = 1.03 (t, 6H, CH_3), 1.58 (m, 4H, CH_2CH_3), 2.26 (m, 4H, CH_2CH_3), 5.36 (t, 2H, HC; *trans*-**15c**), 5.61 (t, 2H, HC; *cis*-**15c**). – ^{13}C NMR ([D$_6$]DMSO): δ = 13.17 (s, CH_3), 18.83 (s, CH_2CH_3), 25.85 (s, $CH_2CH_2CH_3$; *trans*-**15c**), 27.35 (s, $CH_2CH_2CH_3$; *cis*-**15c**), 98.36 (s, ring C atoms; *trans*-**15c**), 99.40 (s, ring C atoms; *cis*-**15c**). – MS (70 eV), *m/z* (%): 241 (9.6) [M$^+$ + 1], 176 (100) [M$^+$ – SO_2]. – $C_8H_{16}O_4S_2$ (240.35): calcd. C 39.98, H 6.71, S 26.68; found C 39.71, H 6.80, S 26.44.

2,4-Di-n-hexyl-1,3-dithietane 1,1,3,3-Tetraoxide (**15e**): Yield 1.87 g (30.2%), m.p. 92 °C. – IR (KBr): ṽ = 2958.3 cm^{-1} (vs), 2932.3 (s), 2859.0 (m), 1345.1 (s), 1334.5 (vs), 1314.3 (s), 1161.9 (s), 1111.8 (s), 1079.0 (m), 682.7 (m). – ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, 6H, 2 CH_3), 1.35 (m, 16H, 2 $C_4H_8CH_3$), 2.26 (m, 4H, 2 $HCCH_2CH_2$), 5.33 (t, 2H, 2 HC). – ^{13}C NMR ($CDCl_3$): δ = 3.7 (s, CH_3), 14.2 (s, CH_2CH_3), 22.6, 26.5, 28.8, 31.4 (each s, C_4H_8), 101.6 (s, ring C atoms). – MS (70 eV), *m/z* (%): 324 (0.1) [M$^+$], 41 (100.0). – $C_{14}H_{28}O_4S_2$ (324.51): calcd. C 51.82, H 8.70, S 19.72; found C 51.80, H 8.78, S 19.87.

2,4-Di-n-nonyl-1,3-dithietane 1,1,3,3-Tetraoxide (**15f**): Yield 2.35 g (29.5%), m.p. 81 °C. – IR (KBr): ṽ = 2965.0 cm^{-1} (w), 2948.6 (m), 2919.7 (vs), 2856.1 (m), 1472.4 (m), 1363.4 (w), 1325.8 (vs), 1158.1 (s), 1080.0 (m), 486.9 (w). – ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 6H, 2 CH_3), 1.29 (m, 28H, 2 $C_7H_{14}CH_3$), 2.26 (m, 4H, 2 $HCCH_2CH_2$), 5.34 (t, 2H, 2 HC). – ^{13}C NMR ($CDCl_3$): δ = 3.7 (s, CH_3), 14.3 (s, CH_2CH_3), 22.9, 26.6, 29.1, 29.2, 29.4, 29.5, 32.0 (each s, C_7H_{14}), 101.6 (s, ring C atoms). – MS (70 eV), *m/z* (%): 408 (0.8) [M$^+$], 83 (100.0). – $C_{20}H_{40}O_4S_2$ (408.67): calcd. C 58.78, H 9.87, S 15.69; found C 58.72, H 10.09, S 15.92.

2,4-Di-n-dodecyl-1,3-dithietane 1,1,3,3-Tetraoxide (**15g**): Yield 2.01 g (21.3%), m.p. 79 °C. – IR (KBr): ṽ = 2949.6 cm^{-1} (s), 2918.8 (vs), 2853.2 (s), 1472.4 (s), 1325.8 (s), 1157.1 (s). – ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, 6H, 2 CH_3), 1.21 (m, 40H, 2 $C_{10}H_{20}CH_3$), 2.20 (m, 4H, 2 $HCCH_2CH_2$), 5.28 (t, 2H, 2 HC). – ^{13}C NMR ($CDCl_3$): δ = 3.7 (s, CH_3), 14.3 (s, CH_2CH_3), 22.9, 26.5, 29.1–32.1 (each s, $C_{10}H_{20}$), 101.6 (s, ring C atoms). – MS (70 eV), *m/z* (%): 492 (0.5) [M$^+$], 43 (100.0). – $C_{26}H_{52}O_4S_2$ (492.83): calcd. C 63.37, H 10.63, S 13.01; found C 63.61, H 10.71, S 13.29.

General Procedure for the Preparation of the Dianions of Alkylated Disulfenes: 5.4 mmol of dialkyldisulfene (**15a–g**) or 2,4,6-trimethyl-1,3,5-trithiane 1,1,3,3,5,5-hexaoxide was suspended in 15 ml of methanol or water. To the suspension was added with stirring 10.8 mmol (16.2 mmol for the hexaoxide) of the corresponding base [KOH, $(CH_3)_4NOH$, $(C_4H_9)_4NOH$, $Bzl(CH_3)_3NOH$] as a 25% aqueous or methanolic solution. The mixture was stirred for 1 h and the solvent was subsequently evaporated. Yields: quantitative.

Dianions **16a** *with Different Cations:*

Dipotassium 2,4-Dimethyl-1,3-dioxo-1λ6,3λ^6-dithiete-1,3-diolate: ^{1}H NMR ([D$_6$]DMSO): δ = 1.19 (s, CH_3), 1.46 (s, CH_3). – ^{13}C NMR ([D$_6$]DMSO): δ = 5.4 (s), 9.9 (s), 179.5 (s, ring C atoms).

Bis(tetramethylammonium) 2,4-Dimethyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate: ^{1}H NMR ([D$_6$]DMSO): δ = 1.2 (s, CH_3), 1.5 (s, CH_3), 3.1 [s, $N(CH_3)_4$].

Bis(tetra-n-butylammonium) 2,4-Dimethyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate: – ^{1}H NMR ([D$_6$]DMSO): δ = 0.93 (s, CH_3), 1.19 (s, $HCCH_3$), 1.30 (m, $N(CH_2CH_2CH_2CH_3)_4$), 1.45 (s, $HCCH_3$), 3.17 [t, $N(CH_2CH_2CH_2CH_3)_4$]. – ^{13}C NMR ([D$_6$]DMSO): δ = 5.5, 9.8 (each s, $HCCH_3$), 23.0, 29.0, 35.7, 57.6 [each s, $N(C_4H_9)_4$].

Bis(benzyltrimethylammonium) 2,4-Dimethyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate: – ^{1}H NMR ([D$_6$]DMSO): δ = 1.19 (s, $HCCH_3$), 1.45 (s, $HCCH_3$), 3.06 [s, $N(CH_2C_6H_5)$], 7.52 (m, phenyl). – ^{13}C NMR ([D$_6$]DMSO): δ = 5.6, 9.9 (each s, $HCCH_3$), 16.9 [s, $N(CH_3)_3$], 71.2 [s, $N(CH_2C_6H_5)$], 126.7–132.8 (each s, phenyl), 185.8 (s, ring C atoms).

Dianions **16b** *with Different Cations:*

Dipotassium 2,4-Diethyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate: ^{1}H NMR ([D$_6$]DMSO): δ = 0.96 (t, CH_3), 1.09 (t, CH_3), 1.70 (q,

CH_2), 2.02 (q, CH_2). – ^{13}C NMR ([D_6]DMSO): δ = 12.9, 13.1 (each s, CH_3), 14.5, 18.7 (each s, CH_2).

Bis(tetramethylammonium) 2,4-diethyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate: ^1H NMR ([D_6]DMSO): δ = 0.96 (s, CH_3), 1.10 (t, CH_3), 1.73 (q, CH_2), 1.97 (q, CH_2), 3.13 [s, $N(CH_3)_4$]. – ^{13}C NMR ([D_6]DMSO): δ = 12.9, 14.7 (each s, CH_3), 18.8, 20.7 (each s, CH_2), 54.3 [each s, $N(CH_3)_4$].

Bis(tetra-n-butylammonium) 2,4-Diethyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate: ^1H NMR ([D_6]DMSO): δ = 0.93 (t, CH_3), 1.19 (q, $HCC\mathit{H}_2$), 1.30 [m, $N(CH_2C\mathit{H}_2C\mathit{H}_2CH_3)_4$], 1.45 (s, $HCC\mathit{H}_2$), 3.17 [t, $N(C\mathit{H}_2CH_2CH_2CH_3)_4$]. – ^{13}C NMR ([D_6]DMSO): δ = 5.5, 9.8 (each s, CH_3), 13.2, 19.1 (each s, $HCCH_2$), 23.0, 29.0, 35.7, 57.6 [each s, $N(C_4H_9)_4$].

Bis(benzyltrimethylammonium) 2,4-Diethyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate: ^1H NMR ([D_6]DMSO): δ = 0.93, 1.12 (each t, CH_3), 1.65, 2.04 (s, $HCC\mathit{H}_2$), 3.06 [s, $N(C\mathit{H}_2C_6H_5)$], 7.52 (m, phenyl). – ^{13}C NMR ([D_6]DMSO): δ = 13.0, 13.2, 14.8 (each s, $H\mathit{C}\mathit{C}H_2CH_3$), 18.9 [s, $N(CH_3)_3$], 71.2 [s, $N(\mathit{C}H_2C_6H_5)$], 128.4–132.8 (each s, phenyl), 158.5 (s, ring C atoms).

Dipotassium 2,4-Di-n-hexyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate (**16e**): ^1H NMR ([D_6]DMSO): δ = 0.90 (t, CH_3), 1.32 [m, $(CH_2)_4$], 2.30 (q, $HCC\mathit{H}_2$).

Dipotassium 2,4-Di-n-nonyl-1,3-dioxo-1λ^6,3λ^6-dithiete-1,3-diolate (**16f**): ^1H NMR ([D_6]DMSO): δ = 0.90 (t, CH_3), 1.32 [m, $(CH_2)_7$], 2.30 (q, $HCC\mathit{H}_2$).

Tripotassium 2,4,6-Trimethyl-1,3,5-trioxo-1λ^6,3λ^6,5λ^6-trithiete-1,3,5-triolate (**17**): ^1H NMR ([D_6]DMSO): δ = 1.57 (s, CH_3). – ^{13}C NMR ([D_6]DMSO): δ = 13.2 (s, CH_3), 184.3 (s, ring C atoms).

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[1] W. Sundermeyer, *Synthesis* **1988**, 349–360.
[2] U. Hartwig, H. Pritzkow, K. Rall, W. Sundermeyer, *Angew. Chem.* **1989**, *101*, 224–225; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 221–223.
[3] U. Rheude, W. Sundermeyer, *Chem. Ber.* **1981**, *114*, 3378–3382.
[4] M. Frasch, W. Sundermeyer, *Chem. Ber.* **1993**, *126*, 537–541.
[5] M. Frasch, W. Sundermeyer, J. Waldi, *Chem. Ber.* **1991**, *124*, 1805–1807.
[6] Y. L. Yagupol'skii, T. I. Savina, *Zh. Org. Khim. (Engl. Transl.)* **1985**, *21*, 1874–1879.
[7] S.-Z. Zhu, D. D. DesMarteau, *Inorg. Chem.* **1993**, *32*, 223–226.
[8] H. R. Mohl, G. Opitz, *Angew. Chem.* **1969**, *81*, 36–37; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 73.
[9] W. Hanefeld, B. Spangenberg, *Chem. Ber.* **1988**, *121*, 1147–1150.
[10] E. Block, E. R. Corey, R. E. Penn, T. L. Renken, P. F. Sherwin, *J. Am. Chem. Soc.* **1976**, *98*, 5715–5717.
[11] B. Balbach, K. Weidenhammer, M. L. Ziegler, *Liebigs Ann. Chem.* **1980**, 1981–1993; B. Balbach, R. Alt, M. L. Ziegler, *Z. Naturforsch. B*, **1982**, *37*, 1005–1013.
[12] E. Block, E. R. Corey, R. E. Penn, T. L. Renken, P. F. Sherwin, H. Bock, T. Hirabayashi, S. Mohmand, *J. Am. Chem. Soc.* **1982**, *104*, 3119–3130.
[13] E. H. Holst, W. C. Fernelius, *J. Org. Chem.* **1958**, *23*, 1881–1883.
[14] P. J. Stang, M. Hanack, L. R. Subramanian, *Synthesis* **1982**, 85–126.
[15] G. Simchen, *in Advances in Silicon Chemistry*, (Ed.: G. Larson), JAI Press, Greenwich, Connecticut, **1991**, p. 189.
[16] M. Frasch, W. Sundermeyer, J. Waldi, *Chem. Ber.* **1992**, *125*, 1763–1767, and refs. cited therein.
[17] Bayer AG (Inventors: U. Finke, H. H. Moretto, H. Niederprüm, H. Vorbrüggen), D.O.S. 2803125, **1979**.
[18] U. Rheude, W. Sundermeyer, *Chem. Ber.* **1983**, *116*, 1285–1296.
[19] A better access is described in the experimental section of this work.
[20] G. Arens, Dissertation, Univ. Heidelberg, **1985**.
[21] E. Baumann, R. Camps, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 69–73.
[22] G. Arens, W. Sundermeyer, H. Pritzkow, *Chem. Ber.* **1986**, *119*, 3631–3638 (more favorable preparation).
[23] P. K. Claus in *Methoden der Organischen Chemie* (Houben-Weyl-Müller), 4. Aufl., Thieme Stuttgart, **1985**, Bd. E 11, S. 1345, 1363, 1412.
[24] M. L. Oftedahl, J. W. Baker, M. W. Dietrich, *J. Org. Chem.* **1965**, 296–298.
[25] H. Stetter, B. Riberi, *Monatsh. f. Chemie* **1972**, *103*, 1262–1270.
[26] N. E. Simpkins, Sulphones in Organic Synthesis, *Tetrahedron Organic Chemistry Series*, Vol. 10, Pergamon Press, New York, **1993**.
[27] H.-J. Gais, J. Vollhardt, C. Krüger, *Angew. Chem.* **1988**, *100*, 1108–1110; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1092–1094, and refs. cited.
[28] G. Boche, *Angew. Chem.* **1989**, *101*, 286–306; *Angew. Chem. Int. Ed. Engl.*, **1989**, *28*, 277–279; and refs. cited.
[29] R. Lett, G. Chassaing, A. Marquett, *J. Organomet. Chem.* **1976**, *111*, C17–C20.

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