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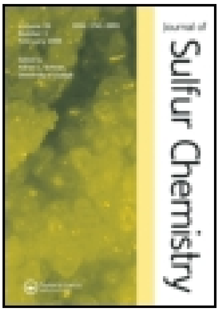

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New aspects of the chemistry of CS_2: synthesis of mercapto-triorganosilyl-thiones by use of tris(trimethylsilyl)methyllithium

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Tris(trimethylsilyl)methyllithium (TsiLi) reacts with CS_2 via cleavage of the C=S double bond and unexpected rearrangement to give sulfur-containing organosilicon compounds. The intermediate, from the reaction between TsiLi and CS_2 is not stable but it has been trapped by various alkyl halides to give mercaptobis-(trimethylsilyl)-thiones. These reactions are quantitative and high yields in short periods of time have been obtained.

Keywords: organosilicon-sulfur; tris(trimethylsilyl)methyllithium; carbon disulfide; mercapto-trimethylsilyl-thione; alkyl halide

1. Introduction

The chemistry of carbon disulfide has been studied extensively. Most reactions proceed via initial nucleophilic attack at carbon.[1–9] According to the literature,[1–4,9–12] the reaction of carbon disulfide with organolithium compounds leads to the formation of intermediates of two types: 1,1-dithioenolates RHC = $C(SLi)_2$ and dithiocarboxylates RC(S)SLi. 1,1-Dithioenolates are ambidentate nucleophiles which react with electrophiles at both sulfur atoms. Dithiocarboxylates in the presence of electrophiles are converted into dithiocarboxylic acid esters, compounds containing one or more C−C(S)S−C groups. Despite the many research publications during the past decade or so that have been concerned with the synthetic applications of CS_2, there are few reports on the reaction of organosilicon compounds with CS_2.[13–15] Therefore, we wish to report reactions of carbon disulfide proceeding by way of nucleophilic attack of tris(trimethylsilyl)methyl anion at the carbon of carbon disulfide.

We have recently used bulky tris(trimethylsilyl)methyllithium (TsiLi) [16] as a reagent in various reactions such as the preparation of vinylsilanes, epoxysilanes, halovinylsilanes, silylethers, etc. In addition, we have investigated its behavior with various electrophiles such as aldehydes,

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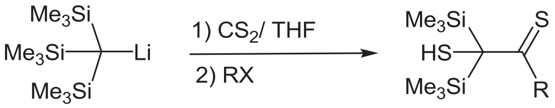
*Corresponding author. Email: dsafa@tabrizu.ac.ir epoxides, benzyl, allyl and alkyl halides.[17–25] With this in mind we have examined the reaction of TsiLi with CS_2 in the presence of various electrophiles in an effort to synthesize products from attack at sulfur. Surprisingly, rearrangement occurred and new organosilicon compounds with thiocarbonyl and mercapto groups were produced. The conversion of carbon disulfide into compounds containing mercapto and thiocarbonyl groups has not previously been observed.

The chemistry of these compounds is considered to be important because compounds containing three different functional groups – trimethylsilyl, mercapto and thiocarbonyl – may be obtained. We name them mercaptobis-(trimethylsilyl)-thiones.

2. Results and discussion

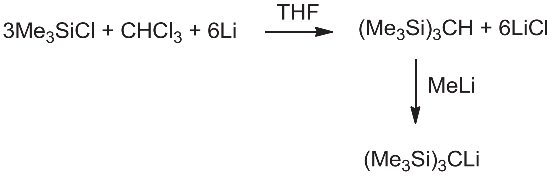
The present report deals with the reaction of tris(trimethylsilyl)methyllithium, carbon disulfide and alkyl halides to give mercaptobis(trimethylsilyl)-thiones (1) (Scheme 1).



(1)

Scheme 1. Reaction of TsiLi and CS_2 with alkyl halides.

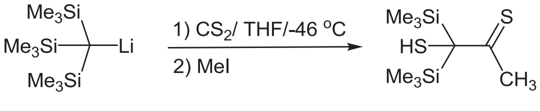
Initially, we chose TsiLi as an organolithium compound and MeI as electrophile. When CS_2 was added to a solution of TsiLi in THF, generated from the reaction of TsiH with MeLi [16] (Scheme 2), at −46°C (cyclohexanone/N_2) and the mixture stirred at the same temperature for 5 min, the color immediately changed from yellow to red, indicating the formation of new anion. Iodomethane was added and the color changed again (back to yellow). The mixture was stirred for 5 min at −46°C and compound **1a** was formed as the sole product in 98% yield (Scheme 3). Its structure was determined from ^{13}C and ^{1}H NMR spectra. A singlet assigned to two trimethylsilyl groups and a broad singlet assigned to the mercapto (SH) proton were detected at 0.14 ppm and 3.18 ppm, respectively. In addition, in the ^{13}C NMR spectrum a very weak peak at 213.6 ppm confirmed the presence of the C=S group.



$$3Me_3SiCl + CHCl_3 + 6Li \xrightarrow{THF} (Me_3Si)_3CH + 6LiCl$$
$$(Me_3Si)_3CH \xrightarrow{MeLi} (Me_3Si)_3CLi$$

Scheme 2. Preparation of tris(trimethylsilyl)methyllithium.

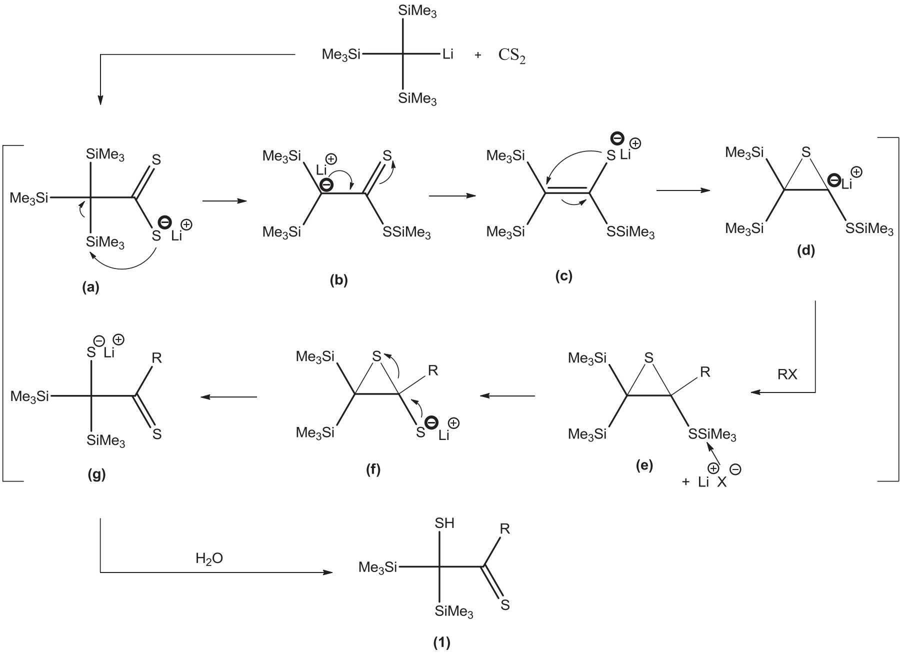
We attempted to separate the intermediate in the reaction of TsiLi with CS_2 but we could not isolate it. Therefore, we decided to trap it with various electrophiles. Although the mechanism is not yet clear, the pathway for the formation of mercaptobis-(trimethylsilyl)-thiones is assumed to be C-to-S migration of the $SiMe_3$ group, then the formation of carbanion (**b**) (thia-Brook rearrangement) [26–29] and, after that, conversion to the enethiolate (**c**).[9,10] The resulting product (**1**) shows that the migration of sulfur to the central carbon of $C(SiMe_3)_2$ has occurred. It



(1a)

Scheme 3. Preparation of 1-mercapto-1,1-bis(trimethylsilyl)propane-2-thione (**1a**).

seems likely that the product (**1**) forms through the intermediates (**d**)–(**g**) and after hydrolysis of (**g**) (Scheme 4).



(1)

Scheme 4. The proposed mechanism of the reaction of TsiLi, CS_2 and alkyl iodide.

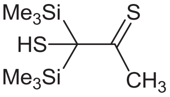
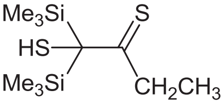
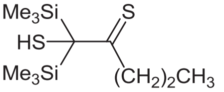
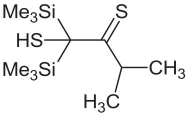
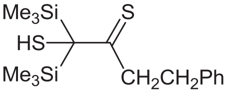
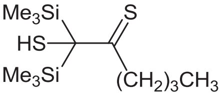
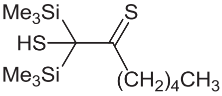
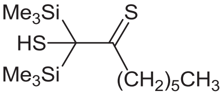
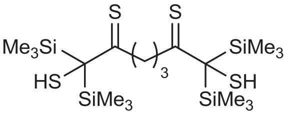
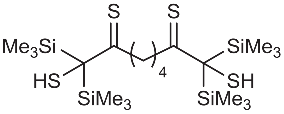
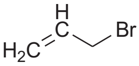
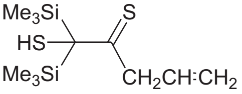
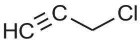
To try to stop the rearrangement, we carried out the reaction with MeI at −78°C and in a one-pot reaction but we obtained the same product (**1a**) in poor yield. To investigate the effect of temperature, the reaction was also carried out at 0°C. A brown solution containing several unidentified products with an unpleasant smell was formed.

After optimizing the reaction conditions, we examined the generality of these conditions in reactions of several symmetrical and unsymmetrical alkyl halides. The results are summarized in Table 1. Progress of the reactions was conveniently monitored by TLC. In all cases, reactions were continued until complete consumption of the initial compounds. Table 1 shows the end time of the reactions and the yields.

Generally, primary alkyl iodides gave higher yields than secondary and tertiary alkyl iodides. 2-Propyl iodide after 1 h gave a poor yield and none of the desired product was detected in the reaction with *tert*-butyl iodide. Reactions of ethyl bromide and *n*-butyl bromide were also investigated. Reaction of TsiLi and CS_2 with alkyl iodides proceeded rapidly, but no reactions were observed with alkyl bromides.

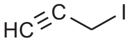
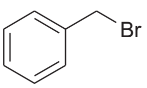
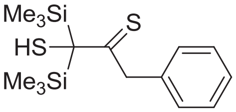
Furthermore, treatment of TsiLi and CS_2 with allyl bromide, benzyl bromide and propargyl halides was investigated. In contrast to the alkyl bromides, the reactions of allyl and benzyl

Table 1. Reaction of TsiLi and CS_2 with various halides.

Entry	RX	Product	Time[a] (min)	Yield[b] (%)
1	CH_3I	 **(1a)**	5	98
2	CH_3CH_2I	 **(1b)**	10	98
3	CH_3CH_2Br	–	60	–
4	$CH_3(CH_2)_2I$	 **(1c)**	15	90
5	CH_3CHICH_3	 **(1d)**	60	Low yield
6	$PhCH_2CH_2Br$	–	60	–
7	$PhCH_2CH_2I$	 **(1e)**	20	85
8	$CH_3(CH_2)_3Br$	–	60	–
9	$CH_3(CH_2)_3I$	 **(1f)**	20	85
10	$(CH_3)_3CI$	–	120	–
11	$CH_3(CH_2)_4I$	 **(1g)**	30	85
12	$CH_3(CH_2)_5I$	 **(1h)**	30	85
13	$ICH_2CH_2CH_2I$	 **(1i)**	45	80
14	$ICH_2(CH_2)_2CH_2I$	 **(1j)**	60	80
15		 **(1k)**	15	98
16		–	120	–

(*Continued*)

Table 1. Continued.

Entry	RX	Product	Time[a] (min)	Yield[b] (%)
17		Unidentified compounds	–	–
18		 **(1l)**	15	98

[a] The reactions were followed by TLC.
[b] Yields obtained by preparative thin layer chromatography (PTLC).

bromides as well as alkyl iodides were quantitative and high yields in short periods of time were obtained. Propargyl chloride and iodide did not show good results. All the products are stable at 0°C for a long time and for several months at room temperature.

3. Conclusion

We have described a novel, efficient and quantitative preparation of a variety of multifunctional mercaptobis(trimethylsilyl)-thiones from the reaction of TsiLi and CS_2 with alkyl, allyl and benzyl halides in THF at −46°C. The intermediate from the reaction between TsiLi and CS_2 was trapped rapidly by alkyl iodides, allyl and benzyl bromide but no reaction was observed with alkyl bromides.

4. Experimental

4.1. *Solvents and reagents*

The reactions were carried out under dry argon. Solvents and CS_2 were dried by standard methods. Substrates for the preparation of tris(trimethylsilyl)methyllithium, namely Me_3SiCl (Merck), Li (Merck), $CHCl_3$ (Merck) and substrates for the preparation of mercaptobis(trimethyl)silylthiones, namely alkyl halides, benzyl and allyl bromide (Merck), *n*-hexane (Merk) for TLC, were used as received. Tris(trimethylsilyl)methyllithium, $(Me_3Si)_3CLi$, was prepared as described by Grobel *et al.*[16] Commercially unavailable alkyl iodides were prepared from alkyl chlorides and bromides as described in the literature.[30]

4.2. *Instrumentation*

The ^1H and ^{13}C NMR were recorded with a Bruker FT-400 MHz spectrometer at room temperature and $CDCl_3$ as a solvent. The mass spectra were obtained with a GC-mass Agilent quadrupole mode 5973N instrument, operating at 70 eV. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were obtained with a Vario EL III instrument.

4.3. *Typical procedure for the preparation of mercaptobis(trimethylsilyl)-thiones (1a–1l)*

To a stirred solution of tris(trimethylsilyl)methyllithium (1 mmol) in THF, carbon disulfide (1.2 mmol) in THF (2 ml) was added at −46°C (cyclohexanone/N_2) under an argon atmosphere.

The mixture was stirred for 5 min and then electrophile (1 mmol) (for compounds **1i** and **1j**, 0.5 mmol of electrophile) was added at this temperature and the stirring was maintained as the mixture was allowed to warm from −46°C to 0°C. The progress of the reaction was followed by TLC with *n*-hexane as solvent. The mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, dried with Na_2SO_4 and filtered. The solvent was evaporated from the filtrate and the residue was purified by preparative TLC on silica gel with *n*-hexane as eluent.

4.3.1. *1-Mercapto-1,1-bis(trimethylsilyl)propane-2-thione (**1a**)*

Yellow liquid, 98% ($R_f = 0.50$). FTIR (KBr, cm^{-1}): 2957 (CH), 1413, 1153 (C=S), 1252, 920 and 837 (C−Si), 1023 (C−S); 1H NMR (400 MHz, $CDCl_3$): δ 0.14 (s, 18H, $SiMe_3$), 2.55 (s, 3H, CH_3), 3.18 (b.s, 1H, SH); ^{13}C NMR ($CDCl_3$): δ −1.21 ($SiMe_3$), 19.76 (CH_3), 55.33 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); m/z (EI): 250 (10%, $[M]^+$), 235 (42%, $[M-CH_3]^+$), 203 (70%, $[HSCC(SiMe_3)_2]^+$), 163 (19%, $[HSCC(SH)SiMe_3]^+$), 115 (61%, $[HSCCSiMe_2]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calcd for $C_9H_{22}S_2Si_2$: C, 43.1; H, 8.8; S, 25.6. Found: C, 43.4; H, 8.6; S, 25.4%.

4.3.2. *1-Mercapto-1,1-bis(trimethylsilyl)butane-2-thione (**1b**)*

Yellow liquid, 98% ($R_f = 0.70$). FTIR (KBr, cm^{-1}): 2960 (CH), 1407, 1152 (C=S), 1251, 918 and 842 (C−Si), 1022 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 18H, $SiMe_3$), 1.27 (t, $J =$ 7.4 Hz, 3H, CH_3), 3.14 (q, $J =$ 7.4 Hz, 3H, CH_2 and SH); ^{13}C NMR ($CDCl_3$): δ −1.18 ($SiMe_3$), 11.79 (CH_3), 30.33 (CH_2), 55.22 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); m/z (EI): 264 (18%, $[M]^+$), 249 (20%, $[M-CH_3]^+$), 203 (68%, $[HSCC(SiMe_3)_2]^+$), 163 (19%, $[HSCC(SH)SiMe_3]^+$), 115 (59%, $[HSCCSiMe_2]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calcd for $C_{10}H_{24}S_2Si_2$: C, 45.4; H, 9.1; S, 24.2. Found: C, 45.6; H, 8.9; S, 24.3%.

4.3.3. *1-Mercapto-1,1-bis(trimethylsilyl)pentane-2-thione (**1c**)*

Yellow liquid, 90% ($R_f = 0.64$). FTIR (KBr, cm^{-1}): 2960 (CH), 1405, 1151 (C=S), 1251, 918 and 840 (C−Si), 1022 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.09 (s, 18H, $SiMe_3$), 0.99 (t, $J =$ 7.3 Hz, 3H, CH_3), 1.61–1.70 (m, 2H, CH_2), 3.13 (t, $J =$ 7.2 Hz, 3H, CH_2 and SH); ^{13}C NMR ($CDCl_3$): δ −1.16 ($SiMe_3$), 12.53 (CH_3), 20.30 and 38.09 (2 × CH_2), 55.40 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); m/z (EI): 278 (5%, $[M]^+$), 277 (10%, $[M\text{-}1]^+$), 235 (20%, $[M-CH_2CH_2CH_3]^+$), 221 (25%, $[S = CC(SH)(SiMe_3)_2]^+$), 163 (39%, $[HSCC(SH)SiMe_3]^+$), 115 (37%, $[HSCCSiMe_2]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calcd for $C_{11}H_{26}S_2Si_2$: C, 47.4; H, 9.4; S, 23.0. Found: C, 47.1; H, 9.6; S, 22.9%.

4.3.4. *1-Mercapto-3-methyl-1,1-bis(trimethylsilyl)butane-2-thione (**1d**)*

Yellow liquid with low yield ($R_f = 0.60$), FTIR (KBr, cm^{-1}): 2960 (CH), 1406, 1151 (C=S), 1252, 919 and 839 (C−Si), 1022 (C−S); m/z (EI): 278 (4%, $[M]^+$), 277 (8%, $[M\text{-}1]^+$), 235 (19%, $[M-CH(CH_3)_2]^+$), 221 (25%, $[S = CC(SH)(SiMe_3)_2]^+$), 163 (39%, $[HSCC(SH)SiMe_3]^+$), 115 (37%, $[HSCCSiMe_2]^+$), 73 (100%, $[SiMe_3]^+$).

4.3.5. *1-Mercapto-4-phenyl-1,1-bis(trimethylsilyl)butane-2-thione (**1e**)*

Yellow liquid, 85%: ($R_f = 0.53$), FTIR (KBr, cm^{-1}): 3064 (Ar), 2959 (CH), 1600–1450 (Ar), 1311, 1158 (C=S), 1250, 916 and 839 (C−Si), 1023 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 18H, $SiMe_3$), 3.19 (t, $J =$ 7.8 Hz, 3H, CH_2 and SH), 3.43 (t, $J =$ 7.8 Hz, 2H, CH_2), 7.19–7.35 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$): δ −1.17 ($SiMe_3$), 33.17 (CH_2), 39.32 (CH_2), 55.40 ($C(SiMe_3)_2SH$), 125.39–127.59 (Ar), 213.62 (C=S, very weak); m/z (EI): 340 (3%, $[M]^+$), 339 (10%, $[M\text{-}1]^+$), 263 (20%, $[M-Ph]^+$), 221 (25%, $[S = CC(SH)(SiMe_3)_2]^+$), 115 (52%, $[HSCCSiMe_2]^+$), 91 (22%, $[\text{benzyl}]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calcd for $C_{16}H_{28}S_2Si_2$: C, 56.4; H, 8.3; S, 18.8. Found: C, 56.5; H, 8.7; S, 18.7%.

4.3.6. *1-Mercapto-1,1-bis(trimethylsilyl)hexane-2-thione (**1f**)*

Yellow liquid, 85% ($R_f = 0.70$), FTIR (KBr, cm^{-1}): 2958 (CH), 1405, 1151 (C=S), 1252, 918 and 841 (C−Si), 1022 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 18H, $SiMe_3$), 0.92 (t, $J = 7.3$ Hz, 3H, CH_3), 1.36–1.46 (m, 2H, CH_2), 1.57–1.64 (m, 2H, CH_2), 3.15 (t, $J = 7.4$ Hz, 3H, CH_2 and SH); ^{13}C NMR ($CDCl_3$): δ −1.17 ($SiMe_3$), 12.66 (CH_3), 21.15, 28.82 and 35.93 ($3 \times CH_2$), 55.40 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); m/z (EI): 292 (3%, $[M]^+$), 291 (6%, $[M\text{-}1]^+$), 235 (10%, $[M-CH_2CH_2CH_2CH_3]^+$), 221 (25%, $[S = CC(SH)(SiMe_3)_2]^+$), 163 (35%, $[HSCC(SH)SiMe_3]^+$), 115 (51%, $[HSCCSiMe_2]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calcd for $C_{12}H_{28}S_2Si_2$: C, 49.2; H, 9.6; S, 21.9. Found: C, 49.4; H, 9.5; S, 22.0%.

4.3.7. *1-Mercapto-1,1-bis(trimethylsilyl)heptane-2-thione (**1g**)*

Yellow liquid, 85% ($R_f = 0.68$), FTIR (KBr, cm^{-1}): 2958 (CH), 1407, 1151 (C=S), 1252, 918 and 836 (C−Si), 1022 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 18H, $SiMe_3$), 0.88 (t, $J = 7.0$ Hz, 3H, CH_3), 1.25–1.40 (m, 4H, $2 \times CH_2$), 1.58–1.65 (m, 2H, CH_2), 3.14 (t, $J = 7.4$ Hz, 3H, CH_2 and SH); ^{13}C NMR ($CDCl_3$): δ −1.18 ($SiMe_3$), 12.93 (CH_3), 21.19, 26.44, 30.12 and 36.16 ($4 \times CH_2$), 55.15 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); m/z (EI): 306 (5%, $[M]^+$), 291 (10%, $[M-CH_3]^+$), 236 (10%, $[M + 1\text{-}CH_2CH_2CH_2CH_2CH_3]^+$), 203 (67%, $[HSCC(SiMe_3)_2]^+$), 163 (18%, $[HSCC(SH)SiMe_3]^+$), 115 (53%, $[HSCCSiMe_2]^+$), 73 (100%, $[SiMe_3]^+$). Anal. Calcd for $C_{13}H_{30}S_2Si_2$: C, 50.9; H, 9.8; S, 20.9. Found: C, 51.2; H, 9.9; S, 20.8%.

4.3.8. *1-Mercapto-1,1-bis(trimethylsilyl)octane-2-thione (**1h**)*

Yellow liquid, 85% ($R_f = 0.82$), FTIR (KBr, cm^{-1}): 2955 (CH), 1408, 1151 (C=S), 1251, 918 and 842 (C−Si), 1022 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 18H, $SiMe_3$), 0.88 (m, 5H, CH_2CH_3), 1.25–1.74 (m, 6H, $3 \times CH_2$), 3.15 (t, $J = 7.4$ Hz, 3H, CH_2 and SH); ^{13}C NMR ($CDCl_3$): δ −1.17 ($SiMe_3$), 13.00 (CH_3), 21.51, 26.71, 27.65, 30.35 and 36.23 ($5 \times CH_2$), 55.17 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); m/z (EI): 320 (5%, $[M]^+$), 305 (10%, $[M-CH_3]^+$), 236 (10%, $[M + 1\text{-}CH_2CH_2CH_2CH_2CH_2CH_3]^+$), 203 (100%, $[HSCC(SiMe_3)_2]^+$), 163 (22%, $[HSCC(SH)SiMe_3]^+$), 115 (63%, $[HSCCSiMe_2]^+$), 73 (99%, $[SiMe_3]^+$). Anal. Calcd for $C_{14}H_{32}S_2Si_2$: C, 52.4; H, 10.0; S, 20.0. Found: C, 52.5; H, 9.7; S, 20.1%.

4.3.9. *1,5-Dimercapto-1,1,5,5-tetrakis(trimethylsilyl)heptane-2,4-dithione (**1i**)*

Yellow liquid, 80% ($R_f = 0.55$), FTIR (KBr, cm^{-1}): 2956 (CH), 1406, 1153 (C=S), 1251, 916 and 841 (C−Si), 1021 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.14 (s, 36H, $SiMe_3$), 1.94–1.98 (m, 2H, CH_2), 3.13 (b.s, 2H, SH), 3.23 (t, $J = 7.1$ Hz, 4H, CH_2); ^{13}C NMR ($CDCl_3$): δ −1.16 ($SiMe_3$), 25.38 and 34.99 ($3 \times CH_2$), 55.41 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); This compound decomposed during GC-mass analysis to give fragments with m/z (EI): 203 ($[HSCC(SiMe_3)_2]^+$), 163 ($[HSCC(SH)SiMe_3]^+$), 115 ($[HSCCSiMe_2]^+$), 73 ($[SiMe_3]^+$). Anal. Calcd for $C_{19}H_{44}S_4Si_4$: C, 44.4; H, 8.6; S, 25.0. Found: C, 44.6; H, 8.8; S, 25.3%.

4.3.10. *1,5-Dimercapto-1,1,5,5-tetrakis(trimethylsilyl)octane-2,4-dithione (**1j**)*

Yellow liquid, 80% ($R_f = 0.50$, m.p.: 72–74°C), FTIR (KBr, cm^{-1}): 2954 (CH), 1403, 1151 (C=S), 1250, 917 and 839 (C–Si), 1021 (C–S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.14 (s, 36H, $SiMe_3$), 1.71–1.74 (m, 4H, CH_2), 3.12 (b.s, 2H, SH), 3.18 (t, 4H, CH_2); ^{13}C NMR ($CDCl_3$): δ -1.16 ($SiMe_3$), 26.20 and 35.46 (4 × CH_2), 55.27 ($C(SiMe_3)_2SH$), 213.62 (C=S, very weak); this compound decomposed during GC-mass analysis to give fragments with m/z (EI): 203 ($[HSCC(SiMe_3)_2]^+$), 163 ($[HSCC(SH)SiMe_3]^+$), 115 ($[HSCCSiMe_2]^+$), 73 ($[SiMe_3]^+$). Anal. Calcd for $C_{20}H_{46}S_4Si_4$: C, 45.5; H, 8.8; S, 24.3. Found: C, 45.6; H, 8.9; S, 24.5%.

4.3.11. *1-Mercapto-1,1-bis(trimethylsilyl)pent-4-ene-2-thione (**1k**)*

Yellow liquid, 98% ($R_f = 0.73$), FTIR (KBr, cm^{-1}): 3084 (CH_{vinyl}), 2954 (CH), 1637 (C=C), 1418, 1153 (C=S), 1250, 917 and 840 (C−Si), 1021 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 18H, $SiMe_3$), 3.13 (b.s, 1H, SH), 3.84 (d, $J = 6.8$ Hz, 2H, CH_2), 5.11 (d, $J = 10.0$ Hz, 1H, CH_2), 5.25 (d, $J = 17.0$ Hz, 1H, CH_2), 5.77–5.87 (m, 1H, CH); ^{13}C NMR ($CDCl_3$): δ -1.17 ($SiMe_3$), 39.20 (CH_2), 55.40 ($C(SiMe_3)_2SH$), 117.31 (CH_{2vinyl}), 130.84 (CH_{vinyl}), 213.60 (C=S, very weak); m/z (EI): 276 (13%, $[M]^+$), 249 (15%, $[M-CH=CH_2]^+$), 203 (13%, $[M-SiMe_3]^+$), 163 (30%, $[HSCC(SH)SiMe_3]^+$), 115 (22%, $[HSCCSiMe_2]^+$), 73 (100%, $[SiMe_3]^+$), 28 (29%, $[CH=CH_2]^+$). Anal. Calcd for $C_{11}H_{24}S_2Si_2$: C, 47.7; H, 8.7; S, 23.2. Found: C, 47.5; H, 8.8; S, 23.1%.

4.3.12. *1-Mercapto-1,1-bis(trimethylsilyl)-3-phenylpropane-2-thione (**1l**)*

Yellow liquid, 98% ($R_f = 0.66$). FTIR (KBr, cm^{-1}): 3065 (Ar), 2957 (CH), 1601–1453 (Ar), 1409, 1150 (C=S), 1252, 917 and 843 (C−Si), 1021 (C−S); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 18H, $SiMe_3$), 3.14 (b.s, 1H, SH), 4.45 (s, 2H, CH_2), 7.28 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$): δ -1.13 ($SiMe_3$), 41.07 (CH_2), 54.94 ($C(SiMe_3)_2SH$), 126.28–135.23 (Ar), 213.62 (C=S, very weak); m/z (EI): 328 (4%, $[M+2]^+$), 327 (6%, $[M+1]^+$), 326 (24%, $[M]^+$), 235 (24%, $[M\text{-benzyl}]^+$), 203 (82%, $[HSCC(SiMe_3)_2]^+$), 115 (45%, $[HSCCSiMe_2]^+$), 91 (100%, $[\text{benzyl}]^+$), 73 (70%, $[SiMe_3]^+$). Anal. Calcd for $C_{15}H_{26}S_2Si_2$: C, 55.1; H, 8.0; S, 19.6. Found: C, 54.9; H, 8.2; S, 19.8%.

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