Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

Synthesis of novel dithiocarbamyl-containing organosilicon compounds

Kazem D. Safa[a], Sama Tavakkoli Osgoei[a] & Maryam Alyari[a]
[a] Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 5166616471 Tabriz, Iran
Published online: 12 Sep 2014.

To cite this article: Kazem D. Safa, Sama Tavakkoli Osgoei & Maryam Alyari (2014) Synthesis of novel dithiocarbamyl-containing organosilicon compounds, Journal of Sulfur Chemistry, 35:6, 683-690, DOI: 10.1080/17415993.2014.953163

To link to this article: http://dx.doi.org/10.1080/17415993.2014.953163

Journal of Sulfur Chemistry, 2014
Vol. 35, No. 6, 683–690, http://dx.doi.org/10.1080/17415993.2014.953163

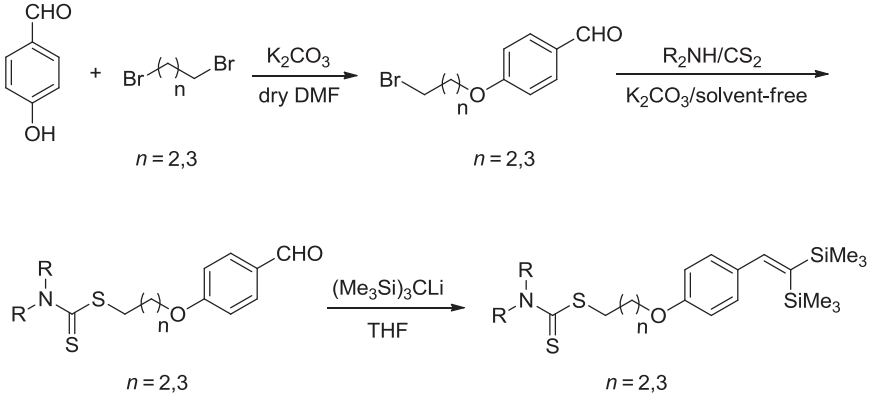
Synthesis of novel dithiocarbamyl-containing organosilicon compounds

Kazem D. Safa*, Sama Tavakkoli Osgoei and Maryam Alyari

Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 5166616471 Tabriz, Iran

(*Received 25 June 2014; accepted 6 August 2014*)

Aldehydes-bearing dithiocarbamate moieties were generated via highly efficient and simple method based on the one-pot reaction of amines, CS_2, and 4-(bromoalkoxy)benzaldehydes with the use of K_2CO_3 as a catalyst under solvent-free conditions. The mild reaction conditions, high yields, and broad scope of the reaction, illustrate the good synthetic utility of this method. The newly synthesized aldehydes were converted to 1,1-bis(trimethylsilyl)-1-alkenes via the Peterson olefination reaction and produced dithiocarbamate-based organosilane compounds.



Keywords: dithiocarbamate; carbon disulfide; tris(trimethylsilyl)methyllithium; 1,1-bis(silyl)-1-alkene; Peterson olefination

1. Introduction

Organic dithiocarbamates have become a field of increasing interest during the past few years.[1,2] They are intensively used as agrochemicals and pharmaceuticals and as intermediates in organic synthesis.[3,4] They can also be found in a variety of biologically active compounds.[5,6] Syntheses of dithiocarbamates involve reactions of amines with CS_2 and alkyl halides or acrylates.[7]

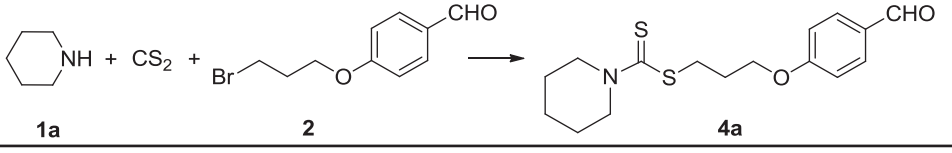
*Corresponding author. Email: dsafa@tabrizu.ac.ir

1,1-bis(silyl)-1-alkenes are useful reagents in organic synthesis because of the presence of Csp^2-Si bonds that undergo numerous transformations. Their use as precursors for the preparation of ketones and isoxazoline derivatives, as well as variety of organosilicon intermediates such as acylsilanes, epoxysilanes, 1-halosilanes, silylenol ethers, (E)-alkenylsilanes, and silylenolacetates, stimulates interest in their synthesis.[8,9] In our previous work, we described the synthesis of β-aminoketones containing bis(trimethylsilyl)ethenyl groups.[10] We have now synthesized a series of dithiocarbamyl-containing organosilicon compounds.

2. Result and discussion

Efficient and safe methods for the synthesis of dithiocarbamates with various substitution patterns at the thiol chain have recently been reported.[11] One method involves the addition of amine to carbon disulfide in the presence of electrophilic reagents,[12] but it suffers from several disadvantages such as the use of strong bases, unsatisfactory yields, high reaction temperatures, and prolonged reaction times. Herein we report a novel, efficient and green synthesis of these compounds under solvent-free conditions by the three-component reaction of amines, carbon disulfide, and 4-(bromoalkoxy)benzaldehydes **2** and **3**. The required starting materials, 4-(3-bromopropoxy)benzaldehyde **2**, and 4-(4-bromobutoxy)benzaldehyde **3** were obtained by the reaction of 4-hydroxy-benzaldehyde and 1,3-dibromopropane or 1,4-dibromo-butane with K_2CO_3 in dry DMF. Initially, the reaction between piperidine **1a** (1 mmol), carbon disulfide (1 mmol), and 4-(3-bromopropoxy)benzaldehyde **2** (1 mmol) in CH_2Cl_2 at room temperature for 1 h without any catalyst, afforded the desired dithiocarbamate **4a** in 40% yield (Table 1, Entry 1). In order to improve the reaction efficiency, we varied the molar ratios of the reactants. When a ratio of 1.5:1:3 (**1a**/**2**/CS_2) was used, the product was isolated in highest yield (Table 1, Entry 4).

Table 1. Synthesis of 3-(4-formylphenoxy)propyl piperidine-1-carbodithioate (**4a**) under different conditions[a].



1a **2** **4a**

Entry	Catalyst (equiv.)	Molar ratio **1a**/**2**/CS_2	Solvent	Time/ min	Yield (%)[b]
1	None	1:1:1	CH_2Cl_2	60	40
2	None	1:1:1	THF	45	43
3	K_2CO_3(0.5)	1.5:1:3	THF	20	89
4	None	1.5:1:3	CH_2Cl_2	40	75
5	K_2CO_3(0.5)	1.5:1:3	CH_2Cl_2	20	82
6	K_2CO_3(0.5)	1.5:1:3	EtOH	14	85
7	None	1.5:1:3	H_2O	8	86
8	None	1.5:1:3	H_2O-EtOH(1:1)	10	83
9	K_2CO_3(0.5)	1.5:1:3	H_2O	7	90
10	K_2CO_3(0.5)	1.5:1:3	H_2O-EtOH(1:1)	9	87
11	K_2CO_3(0.5)	1.5:1:3	H_2O(60°C)	5	92
12	K_2CO_3(0.5)	1.5:1:3	H_2O	7	93
13	None	1:1:1	Solvent-free	18	63
14	None	1.5:1:3	Solvent-free	5	91
15	K_2CO_3(0.5)	1.5:1:3	Solvent-free	3	94

[a]All reactions were carried out at open atmosphere.
[b]Isolated yield based on **4a**.

When water was used as the alternative medium of CH_2Cl_2, a similarly good result was obtained (Table 1, Entry 7).

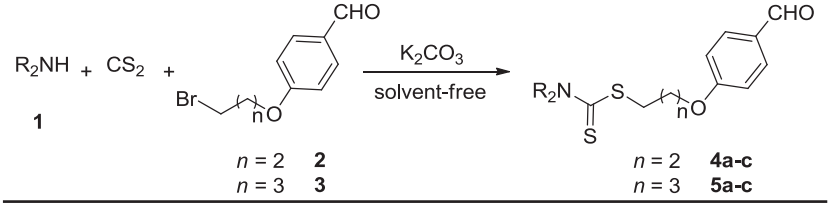
With 0.5 mmol K_2CO_3 as catalyst, the process is driven rapidly to completion (Table 2, Entry 9) and only one equivalent of amine is required.[11] Without solvent at room temperature the one-pot reaction gave the dithiocarbamate in excellent yield with K_2CO_3 as a catalyst. The reaction conditions were finally established as given in Entry 15 (Table 1). The addition of amine to CS_2 was slow, maintaining the temperature at around 0°C followed by the addition of 4-(bromopropoxy)benzaldehyde **2** or 4-(bromobutoxy)benzaldehyde **3** at room temperature. Generally, the solvent-free reaction is fast, experimentally simple, gives higher selectivity, and generates virtually no by-products.

To show the generality and scope of this new protocol, structurally diverse amines were treated with 4-(bromoalkoxy)benzaldehydes and the results are shown in Table 2. By using solvent-free conditions, the corresponding products were afforded in good to excellent yield (Table 2).

Recently, we have embarked on a program directed toward the use of tris(trimethylsilyl) methane, $(Me_3Si)_3CH$, for the generation of synthetically useful organosilicon compounds.[13,14] To extend this reaction to the synthesis of dithiocarbamates bearing organosilicon groups, the newly synthesized aldehydes were treated with $(Me_3Si)_3CLi$, and the related 2-aryl-1,1-bis(silyl)alkenes were produced in good yields (Scheme 1, Table 3). 2-Aryl-1,1-bis(silyl)alkenes represent an important class of key compounds that have been used for various applications, especially as synthetic intermediates.[15,16]

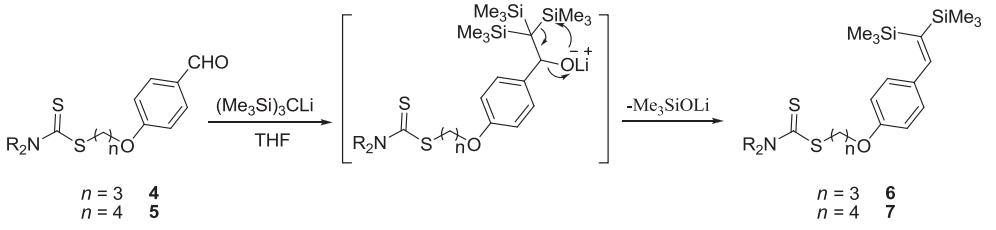
The organolithium reagent, $(Me_3Si)_3CLi$, was made by deprotonation of $(Me_3Si)_3CH$ by MeLi under reflux conditions in THF. The starting precursor tris(trimethylsilyl)methane has been conveniently prepared by the reaction between $CHCl_3$ and Li with Me_3SiCl in THF.[17]

Table 2. One-pot synthesis of (4-formylphenoxy)butyl(propyl) dialkylcarbamodithioate under solvent-free conditions.



Entry	Amine **1**	Aldehyde	Product	Time/min	Yield (%)[a]
1	Piperidine **1a**	**2**	**4a**	3	94
2	Piperidine **1a**	**3**	**5a**	3	94
3	Dipropylamine **1b**	**2**	**4b**	4	93
4	Dipropylamine **1b**	**3**	**5b**	4	92
5	Diisopropylamine **1c**	**2**	**4c**	3	93
6	Diisopropylamine **1c**	**3**	**5c**	4	94

[a]Isolated yield.



Scheme 1. Synthesis of dithiocarbamyl-containing organosilicon compounds.

Table 3. The results of the preparation of 2-aryl-1,1-bis(silyl)alkenes containing dithiocarbamates.

Entry	Aldehyde	R_2N-	Product	Time/min	Yield (%)[a]
1	**4a**	Piperidine	**6a**	6	92
2	**5a**	Piperidine	**7a**	5	93
3	**4b**	Dipropylamine	**6b**	7	91
4	**5b**	Dipropylamine	**7b**	6	92
5	**4c**	Diisopropylamine	**6c**	6	92
6	**5c**	Diisopropylamine	**7c**	5	93

[a]Isolated yield.

The reaction is carried out, with stirring, at room temperature. All the newly synthesized compounds were characterized through spectroscopic techniques. The ^{1}H NMR spectra of the **6a** show the complete disappearance of aldehydic proton resonance and the concomitant appearance of signals assigned to HC=C at 7.68 ppm and -$SiMe_3$ protons at −0.01 and 0.18 ppm. Similar results were observed for **6b**, **6c** and **7a–c**.

3. Conclusion

We demonstrated the convenient one-pot and solvent-free preparation of various dithiocarbamates by a facile reaction of 4-(3-bromoalkoxy)benzaldehydes, carbon disulfide and a amine under solvent-free conditions at room temperature. The significant advantages offered by this protocol are simple operation, easy accessibility of reactants, no solvent, reaction at room temperature (energy efficient), and high yields of products. The newly synthetic dithiocarbamates containing formyl group were obtained from the reaction of $(Me_3Si)_3CLi$ with variety of dithiocarbamates. These compounds might be used as intermediate for the synthesis of attractive molecules containing organosilicon groups.

4. Experimental

4.1. *Solvents and reagents*

Reactions involving organolithium reagents 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, Li, $CHCl_3$, and substrates for the preparation of 4-(bromoalkoxy)benzaldehydes, namely, 4-hydroxy-benzaldehyde, 1,4-dibromo-butane, 1,3-dibromo-propane, K_2CO_3, and DMF were purchased from Merck and Fluka.

4.2. *Instrumentation*

The ^{1}H NMR and ^{13}C NMR were recorded with a Bruker FT-400 MHz spectrometer at room temperature and $CDCl_3$ as a solvent. The FTIR spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were carried out with a Heareus CHN-ORAPID instrument.

4.3. *General procedure for the preparation of 4-(3-bromopropoxy)benzaldehyde 2 and 4-(4-bromobutoxy)benzaldehyde 3*

To a stirred solution of 4-hydroxy-benzaldehyde (1 g, 8.2 mmol) in dry DMF (30 mL), K_2CO_3 (1.70 g, 12.3 mmol) and 1,3-dibromopropane or 1,4-dibromo-butane (81.9 mmol) were added

consecutively. The mixture was stirred at room temperature for 24 h. Then DMF was evaporated in vacuum, and the residue was taken up in CH_2Cl_2 and washed with H_2O. The organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. After filtration, the solvent was evaporated, and the residue was purified by column chromatography (*n*-hexane/ethyl acetate, 4:1, $R_f = 0.80$) for **2** and (*n*-hexane/ethyl acetate, 4:1, $R_f = 0.76$) for **3**. The compounds have been described previously.[18,19]

4.4. *General procedure for the preparation of 4-(4-formylphenoxy)butyl dialkylcarbamodithioate and 3-(4-formylphenoxy)propyl dialkylcarbamodithioate*

To a well stirred mixture of 4-(3-bromopropoxy)benzaldehyde or 4-(4-bromobutoxy)benzaldehyde (1 mmol) with CS_2 (1 mmol) was added secondary amine drop-wise over 2 min at 0°C, and the stirring was continued for 3 min at 0°C. The mixture was allowed to warm to room temperature, then stirred until the reaction was shown by TLC to be complete. The reaction mixture was then poured into distilled water (30 ml) and extracted with dichloromethane. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by preparative TLC on silica gel using *n*-hexane and dichloromethane as eluent to give the product.

4.4.1. *3-(4-formylphenoxy)propyl piperidine-1-carbodithioate (**4a**)*

Yellow solid, 94% ($R_f = 0.33$), m.p. 70–72°C. FTIR (KBr, cm^{-1}): 2740, 1682 (C=O), 1465, 1154 (C=S), 1025 (C–S), 837; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62–1.75 (m, 6H), 2.22–2.29 (m, 2H, CH_2), 3.51 (t, $J = 7.1$ Hz, 2H, CH_2–S), 3.89 (bs, 2H, CH_2–N), 4.15 (t, $J = 6.1$ Hz, 2H, CH_2–O), 4.29 (bs, 2H, CH_2–N), 7.00 (d, $J = 8.7$ Hz, 2H, Ar), 7.83 (d, $J = 8.7$ Hz, 2H, Ar), 9.88 (s, 1H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.27, 24.50, 24.98, 27.55, 32.25, 50.31, 51.93, 65.79, 113.76, 128.89, 130.98, 162.89, 189.83 (C=O), 194.09 (C=S); Anal. Calcd for $C_{16}H_{21}NO_2S_2$: C, 59.41; H, 6.54; N, 4.33. Found: C, 59.58%; H, 6.63%; N, 4.19%.

4.4.2. *4-(4-formylphenoxy)butyl piperidine-1-carbodithioate (**5a**)*

Yellow solid, 94% ($R_f = 0.52$), m.p. 44–46°C. FTIR (KBr, cm^{-1}): 2735, 1687 (C=O), 1425, 1158 (C=S), 1008 (C–S), 830; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60–1.73 (m, 6H), 1.86–1.97 (m 4H), 3.37 (t, $J = 7.0$ Hz, 2H, CH_2–S), 3.87 (bs, 2H, CH_2–N), 4.06 (t, $J = 6.0$ Hz, 2H, CH_2–S), 4.27 (bs, 2H, CH_2–N), 6.97 (d, $J = 8.6$ Hz, 2H, Ar), 7.80 (d, $J = 8.6$ Hz, 2H, Ar), 9.85 (s, 1H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.19, 24.41, 24.89, 27.16, 35.48, 50.16, 51.79, 66.66, 113.65, 128.69, 130.88, 162.94, 189.74 (C=O), 194.36 (C=S); Anal. Calcd for $C_{17}H_{23}NO_2S_2$: C, 60.50; H, 6.87; N, 4.15. Found: C, 60.65%; H, 6.98%; N, 3.99%.

4.4.3. *3-(4-formylphenoxy)propyl dipropylcarbamodithioate (**4b**)*

Yellow solid, 93% ($R_f = 0.40$), m.p. 76–78°C. FTIR (KBr, cm^{-1}): 2736, 1691 (C=O), 1480, 1159 (C=S), 1029 (C–S), 832; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90–0.96 (m, 6H), 1.70–1.83 (m, 4H), 2.20–2.26 (m, 2H), 3.47 (t, $J = 7.1$ Hz, 2H, CH_2-S), 3.58–3.63 (m, 2H, CH_2–N), 3.88–3.92 (m, 2H, CH_2–N), 4.14 (t, $J = 6.1$ Hz, 2H, CH_2-O), 6.99 (d, $J = 8.6$ Hz, 2H, Ar), 7.82 (d, $J = 8.6$ Hz, 2H, Ar), 9.87 (s, 1H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.15, 18.56, 19.60, 27.43, 32.24, 53.26, 55.78, 65.79, 113.71, 128.83, 130.91, 162.84, 189.75 (C=O), 194.58 (C=S); Anal. Calcd for $C_{17}H_{25}NO_2S_2$: C, 60.14; H, 7.42; N, 4.13. Found: C, 60.26%; H, 7.58%; N, 3.94%.

4.4.4. *4-(4-formylphenoxy)butyl dipropylcarbamodithioate (**5b**)*

Yellow solid, 92% ($R_f = 0.43$), m.p. 49–51°C. FTIR (KBr, cm^{-1}): 2734, 1691(C=O), 1475, 1156 (C=S), 1030 (C-S), 831; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91–0.96 (m, 6H), 1.72–1.74 (m, 4H), 1.86–1.98 (m, 4H), 3.36 (t, $J = 7.0$ Hz, 2H, CH_2–S), 3.61 (t, $J = 7.9$ Hz, 2H, CH_2–N), 3.90 (t, $J = 7.8$ Hz, 2H, CH_2–N), 4.08 (t, $J = 6.0$ Hz, 2H, CH_2–O), 6.98 (d, $J = 8.7$ Hz, 2H, Ar), 7.81 (d, $J = 8.7$ Hz, 2H, Ar), 9.87 (s, 1H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.17, 18.63, 19.62, 24.40, 27.26, 35.61, 53.26, 55.76, 66.74, 113.73, 128.82, 130.93, 163.02, 189.74 (C=O), 195.05 (C=S); Anal. Calcd for $C_{18}H_{27}NO_2S_2$: C, 61.15; H, 7.70; N, 3.96. Found: C, 61.28%; H, 7.92%; N, 3.75%.

4.4.5. *3-(4-formylphenoxy)propyl diisopropylcarbamodithioate (**4c**)*

Yellow solid, 93% ($R_f = 0.46$), m.p. 73–75°C. FTIR (KBr, cm^{-1}): 2729, 1689 (C=O), 1475, 1155 (C=S), 1030 (C–S), 836; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24–1.64 (m, 12H), 1.89–1.98 (m, 2H,–CH_2), 2.21–2.28 (m, 2H), 3.48 (bs, 2H, CH_2–N), 4.15 (t, 2H, $J = 6.2$ Hz, CH_2–O), 7.00 (d, $J = 8.7$ Hz, 2H, Ar), 7.82 (d, $J = 8.7$ Hz, Ar), 9.87 (s, 1H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.74, 27.34, 65.94, 66.74, 113.75, 128.85, 130.95, 162.91, 189.80 (C=O), 194.98 (C=S); Anal. Calcd for $C_{17}H_{25}NO_2S_2$: C, 60.14; H, 7.42; N, 4.13. Found: C, 60.29%; H, 7.60%; N, 3.96%.

4.4.6. *4-(4-formylphenoxy)butyl diisopropylcarbamodithioate (**5c**)*

Yellow solid, 94% ($R_f = 0.52$), m.p. 41–43°C. FTIR (KBr, cm^{-1}): 2734, 1689 (C=O), 1438, 1162 (C=S), 1031 (C–S), 831; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24–1.62 (m, 14H), 1.91–2.00 (m, 4H), 3.38 (bs, 2H), 4.08 (t, $J = 6.0$ Hz, CH_2–O), 6.98 (d, $J = 8.7$ Hz, 2H, Ar), 7.82 (d, $J = 8.7$ Hz, 2H, Ar), 9.87 (s, 1H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.80, 24.19, 27.37, 66.21, 66.75, 113.72, 128.77, 130.96, 163.04, 189.83 (C=O), 194.36 (C=S); Anal. Calcd for $C_{18}H_{27}NO_2S_2$: C, 61.15; H, 7.70; N, 3.96. Found: C, 61.32%; H, 7.98%; N, 3.73%.

4.5. *General procedure for the preparation of 3-(4-(2,2-bis(trimethylsilyl)vinyl)phenoxy)propyl dialkylcarbamodithioate*

To a stirred solution of tris(trimethylsilyl)methyllithium (1 mmol) in THF, 4-(4-formylphenoxy) butyl dialkylcarbamodithioate or 3-(4-formylphenoxy)propyl dialkylcarbamodithioate (1 mmol) in 2 mL THF was added at room temperature under argon atmosphere. The progress of the reaction was followed by TLC with *n*-hexane as eluent. After completion of the reaction, the mixture is poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over Na_2SO_4, and filtered. The solvent was evaporated and the residue was purified by preparative TLC on silica gel using *n*-hexane as eluent to give the product.

4.5.1. *3-(4-(2,2-bis(trimethylsilyl)vinyl)phenoxy)propyl piperidine-1-carbodithioate (**6a**)*

Yellow oil, 92% ($R_f = 0.76$). FTIR (KBr, cm^{-1}): 2862 (=CH–), 1244 and 837 (C–Si), 1171 (C=S); ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.01 (s, 9H, $SiMe_3$), 0.18 (s, 9H, $SiMe_3$), 1.65–1.75 (m, 6H), 2.18–2.25 (m, 2H), 3.50 (t, $J = 7.1$ Hz, CH_2–S), 3.90 (bs, 2H, CH_2–N), 4.07 (t, $J = 6.1$ Hz, 2H, CH_2–O), 4.30 (bs, 2H, CH_2–N), 6.82 (d, $J = 8.6$ Hz, 2H, Ar), 7.11 (d, $J = 8.6$ Hz, 2H, Ar), 7.68 (s, 1H, 9CH–); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.402 ($SiMe_3$), 1.091 ($SiMe_3$), 23.31, 24.53, 24.95, 27.55, 27.74, 32.55, 35.82, 50.30, 51.82, 65.42, 66.34, 112.69, 128.18, 134.20,

143.86, 153.61, 157.07, 194.47 (C=S); Anal. Calcd for $C_{23}H_{39}NOS_2Si_2$: C, 59.30; H, 8.44; N, 3.01. Found: C, 59.53%; H, 8.67%; N, 2.78%.

4.5.2. *4-(4-(2,2-bis(trimethylsilyl)vinyl)phenoxy)butyl piperidine-1-carbodithioate (**7a**)*

Yellow oil, 93% ($R_f = 0.76$). FTIR (KBr, cm^{-1}): 2861 (=CH–), 1171 (C=S), 1244 and 838 (C–Si), 1014 (C–S); ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.02 (s, 9H, $SiMe_3$), 0.17 (s, 9H, $SiMe_3$), 1.65–1.75 (m, 6H), 1.91–1.92 (m, 4H, CH_2), 3.39 (t, $J = 6.7$ Hz, 2H, CH_2–S), 3.90 (bs, 2H), 3.97 (t, $J = 5.6$ Hz, 2H, CH_2–O), 4.301 (bs, 2H), 6.81 (d, $J = 8.5$ Hz, 2H, Ar), 7.10 (d, $J = 8.5$ Hz, 2H, Ar), 7.67 (s, 1H, = CH–); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.41 ($SiMe_3$), 1.08 ($SiMe_3$), 23.31, 24.51, 27.53, 35.80, 66.30, 112.62, 128.16, 134.05, 143.75, 153.62, 157.14, 194.68 (C=S); Anal. Calcd for $C_{24}H_{41}NOS_2Si_2$: C, 60.07; H, 8.61; N, 2.92. Found: C, 60.27%; H, 8.88%; N, 2.73%.

4.5.3. *3-(4-(2,2-bis(trimethylsilyl)vinyl)phenoxy)propyl dipropylcarbamodithioate (**6b**)*

Yellow oil, 91% (R_f = 0.72). FTIR (KBr, cm^{-1}): 2855 (=CH–), 1172 (C=S), 1247 and 836 (C–Si), 1025 (C–S); ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.02 (s, 9H, $SiMe_3$), 0.17 (s, 9H, $SiMe_3$), 1.25–1.33 (m, 6H), 1.51–1.58 (m, 4H), 2.01–2.06 (m, 2H), 3.41 (t, $J = 7.3$ Hz, 2H, CH_2–S), 3.49–3.54 (m, 2H, CH_2–N), 3.81–3.89 (m, 2H, CH_2–N), 4.10 (t, $J = 6.2$ Hz, 2H, CH_2–O), 6.84 (d, $J = 8.5$ Hz, Ar), 7.11 (d, $J = 8.5$ Hz, Ar), 7.68 (s, 1H, 9CH–); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.41, 1.06, 10.17, 17.84, 19.70, 29.39, 34.12, 54.01, 56.24, 67.76, 112.87, 116.67, 128.16, 133.46, 153.54 (C=O), 195.24 (C=S); Anal. Calcd for $C_{24}H_{43}NOS_2Si_2$: C, 59.82; H, 8.99; N, 2.91. Found: C, 60.02%; H, 9.20%; N, 2.73%.

4.5.4. *4-(4-(2,2-bis(trimethylsilyl)vinyl)phenoxy)butyl dipropylcarbamodithioate (**7b**)*

Yellow sticky solid, 92% ($R_f = 0.73$). FTIR (KBr, cm^{-1}): 2873 (=CH–), 1172 (C=S), 1244 and 836 (C–Si), 1033 (C–S); ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.02 (s, 9H, $SiMe_3$), 0.17 (s, 9H, $SiMe_3$), 0.92–0.97 (m, 6H), 1.73–1.77 (m, 4H), 1.90–1.92 (m, 4H), 3.36 (t, $J = 6.8$ Hz, 2H, CH_2–S), 3.63 (t, $J = 7.8$ Hz, 2H), 3.91 (t, $J = 7.8$ Hz, 2H), 3.99 (t, $J = 5.6$ Hz, 2H, CH_2–O), 6.81 (d, $J = 8.5$ Hz, 2H, Ar), 7.10 (d, $J = 8.5$ Hz, 2H, Ar), 7.68 (s, 1H, =CH–); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.41 ($SiMe_3$), 1.08 ($SiMe_3$), 10.21, 18.65, 19.62, 24.42, 27.57, 35.86, 53.28, 55.74, 66.32, 112.63, 128.16, 134.06, 143.76, 153.64, 157.16, 195.22 (C=S); Anal. Calcd for $C_{25}H_{45}NOS_2Si_2$: C, 60.55; H, 9.15; N, 2.82. Found: C, 60.68%; H, 9.31%; N, 2.68%.

4.5.5. *3-(4-(2,2-bis(trimethylsilyl)vinyl)phenoxy)propyl diisopropylcarbamodithioate (**6c**)*

Yellow oil, 92% ($R_f = 0.66$). FTIR (KBr, cm^{-1}): 2871 (=CH–), 1174 (C=S), 1247 and 842 (C–Si), 1036 (C–S); ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.01 (s, 9H, $SiMe_3$), 0.17 (s, 9H, $SiMe_3$), 1.21–1.68 (m, 15H), 2.20–2.23 (m, 2H), 3.48 (bs, 2H), 4.05 (t, $J = 6.2$ Hz, 2H, CH_2–O), 6.82 (d, $J = 8.6$ Hz, 2H, Ar), 7.11 (d, $J = 8.6$ Hz, 2H, Ar), 7.67 (s, 1H, =CH–); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.42 ($SiMe_3$), 1.07 ($SiMe_3$), 18.77, 24.86, 27.64, 65.48, 66.28, 112.61, 128.13, 134.08, 143.75, 153.57, 157.03, 194.05 (C=S); Anal. Calcd for $C_{24}H_{43}NOS_2Si_2$: C, 59.82; H, 8.99; N, 2.91. Found: C, 59.96%; H, 9.13%; N, 2.78%.

4.5.6. *4-(4-(2,2-bis(trimethylsilyl)vinyl)phenoxy)butyl diisopropylcarbamodithioate (**7c**)*

Yellow oil, 93% ($R_f = 0.64$). FTIR (KBr, cm^{-1}): 2883 (=CH–), 1246 and 836 (C–Si), 1170 (C=S), 1033 (C–S); ^{1}H NMR (400 MHz, $CDCl_3$): δ −0.02 (s, 9H, $SiMe_3$), 0.17 (s, 9H, $SiMe_3$), 1.41–1.42 (m, 12H), 1.91–1.92 (m, 4H), 2.90 (t, $J = 6.2$ Hz, 2H, CH_2–S), 3.38 (bs, 2H), 4.00 (t, $J = 5.9$ Hz, 2H, CH_2–O), 6.81 (d, $J = 8.5$ Hz, 2H, Ar), 7.10 (d, $J = 8.5$ Hz, 2H, Ar), 7.67 (s, 1H, =CH–); ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.41 ($SiMe_3$), 1.08 ($SiMe_3$), 19.63, 19.92, 24.20, 27.67, 66.32, 112.61, 128.15, 134.03, 143.73, 153.63, 157.16, 193.97 (C=S); Anal. Calcd for $C_{25}H_{45}NOS_2Si_2$: C, 60.55; H, 9.15; N, 2.82. Found: C, 60.72%; H, 9.30%; N, 2.69%.

Acknowledgements

We thank Dr. N. Arsalani for supplying some of the starting materials.

References

[1] Azizi N, Pourhasan B, Aryanasab F, Saidi MR. A simple and novel eco-friendly process for one-pot synthesis of dithiocarbamates from amines, carbon disulfide, and epoxides. Synlett. 2007;8:1239–1242.
[2] Azizi N, Pourhasan B, Aryanasab F, Saidi MR. Straightforward and highly efficient catalyst-free one-pot synthesis of dithiocarbamates under solvent-free conditions. Org Lett. 2006;8:5275–5277.
[3] Goubert-Renaudin S, Schneider R, Walcarius A. Synthesis of new dithiocarbamate-based organosilanes for grafting on silica. Tetrahedron Lett. 2007;48:2113–2116.
[4] Movassagh B, Shokri B. A facile and efficient one-pot regioselective synthesis of 2-hydroxyalkyl dithiocarbamates under catalyst-free conditions. Int J Org Chem. 2012;2:248–253.
[5] Bardajee GR, Sadraei S, Taimoory SM, Abtin E. One-pot synthesis of dithiocarbamates under solvent-free conditions in the presence of KF/Al_2O_3. Asian J Biochem Pharm Res. 2011;1:178–184.
[6] Chaturvedi D, Ray S. An efficient, one-pot, synthesis of dithiocarbamates from the corresponding alcohols using Mitsunobu's reagent. Tetrahedron Lett. 2006;47:1307–1309.
[7] Chatterjee T, Bhadra S, Ranu BC. Transition metal-free procedure for the synthesis of s-aryl dithiocarbamates using aryl diazonium fluroborate in water at room temperature. Green Chem. 2011;13:1837–1842.
[8] Pawluc P, Hreczycho G, Walkowia J, Marciniec B. A new facile synthesis of 1,1-dibromo-2-arylethenes. Synlett. 2007;13:2061–2064.
[9] Hreczycho G, Pawluc P, Marciniec B. An efficient synthesis of unsymmetrical 1,1-bis(silyl)ethenes. Synthesis. 2006;8:1370–1374.
[10] Safa KD, Abolfathi M, Ghorbanpour Kh. Synthesis of β-amino ketones containing organosilicon groups: catalytic enantioselective three-component Mannich-type reaction. J Chem Res. 2012;36:575–578.
[11] Rudorf W-D. Reaction of carbon disulfide with N-nucleophiles. J Sulfur Chem. 2007;28:295–339.
[12] Tellez F, Cruz A, Lopez-Sandoval H, Ramos-Garcia I, Gayosso M, Castillo-Sierra RN, Paz-Michel B, Nöth H, Flores-Parra A, Contreras R. Dithiocarbamates, thiocarbamic esters, dithiocarboimidates, guanidines, thioureas, isothioureas, and tetraazathiapentalene derived from 2-aminobenzothiazole. Eur J Org Chem. 2004;7(20):4203–4214.
[13] Safa KD, Ghorbanpour Kh. New aspects of the chemistry of CS_2: synthesis of Mercapto-triorganosilyl-thiones by use of tris(trimethylsilyl)methyllithium. J Sulfur Chem. 2014;35(2):170–178.
[14] Safa KD, Mosaei YO. Functionalization of the upper rim of calyx[4]arene via alcoholysis and hydrosilylation reactions. J Organomet Chem. 2010;695:505–511.
[15] Safa KD, Ghorbanpour Kh, Hassanpour A, Tofangdarzadeh Sh. 1,4-bis[2,2-bis(trimethylsilyl)ethenyl]benzene: regioselective ring opening of its a,b-epoxybis(silane) with some nucleophiles. J Organomet Chem. 2009;694:1907–1911.
[16] Safa KD, Namvari M, Hassanpour A, Tofangdarzadeh Sh. Synthesis and desilylation of some bis(trimethylsilyl) alkenes and polymers bearing bis(silyl)alkenyl groups. J Organomet Chem. 2009;694:2448–2453.
[17] Eaborn C. The novel chemistry of compounds with tris(trimethylsilyl)methyl or related ligands on silicon. J Chem Soc Dalton Trans. 2001;30(23):3397–3406.
[18] Moutevelis-Minakakis P, Papavassilopoulou E, Mavromoustakos T. Synthesis of new optically active 2-pyrrolidinones. Molecules. 2013;18:50–73.
[19] Pan L-F, Wang X-B, Xie S-S, Li S-Y, Kong L-Y. Multitarget-directed resveratrol derivatives: anti-cholinesterases, anti-β-amyloid aggregation and monoamine oxidase inhibition properties against Alzheimer's disease. Med Chem Commun. 2014;5:609–616.