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Synthesis of primary thiocarbamates by silica sulfuric acid as effective reagent under solid-state and solution conditions

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HIGHLIGHTS

- A green and simple method for the conversion of alcohols and phenols to primary *O*-thiocarbamates and *S*-thiocarbamates.
- Using of silica sulfuric acid ($\equiv SiO_2—OSO_3H$) as a solid acid in the absence of solvent (solvent-free condition).
- To report X-ray data of primary *O*-thiocarbamate and *S*-thiocarbamate for the first time.

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ABSTRACT

A simple and efficient method for the conversion of alcohols and phenols to primary *O*-thiocarbamates and *S*-thiocarbamates in the absence of solvent (solvent-free condition) using silica sulfuric acid ($\equiv SiO_2—OSO_3H$) as a solid acid is described. The products are easily distinguished by IR, NMR and X-ray data. X-ray data of the compounds reveal a planar trigonal orientation of the NH_2 nitrogen atom with the partial C,N double-bond character and the C=S or C=O groups in *syn*periplanar position with $C_{aryl}—O$ and $C_{alkyl}—S$ moieties, respectively. Moreover, the —O—CS—NH_2 group which is perpendicular to the plane of the benzene ring in **1c** and the central thiocarbamate —S—CO—NH_2 group in **2b** are essentially planar.

1. Introduction

Thiocarbamates are esters of thiocarbamic acids, the generic name has been indiscriminately given to the tautomeric species with the general formula $R^1SC(O)NR^2R^3$ or $R^1OC(S)NR^2R^3$ (R^1 typically is an alkyl or an aryl group attached to the sulfur – giving *S*-thiocarbamates – or to the oxygen – giving *O*-thiocarbamates). Thiocarbamates have received much attention due to their interesting technological, biological and synthetic applications [1–18].

Traditionally, secondary and tertiary thiocarbamates were obtained by several-pot reaction methods [1,4–8,14–32]. The most widely utilized method for the synthesis of them uses phosgene or thiophosgene (and their substituted derivatives) as a reagent in organic solvents. They are highly toxic reagents and hazardous to handle, especially in large-scale preparations [1,33,34]. The used organic solvents are toxic and are not eco-friendly. From the standpoint of 'green chemistry', significant efforts have been made to find alternatives to organic solvents. A very attractive substitute for these solvents is given in solvent–free reactions [35–37]. It is industrially important due to reduced pollution, low costs, and simplicity in process and handling. Therefore the conventional method involves environmental and safety problems. Owing to the above mentioned facts, much effort has been directed toward alternative routes for preparation of thiocarbamates.

Furthermore, these methods cannot produce *N*-unsubstituted thiocarbamates. While the secondary and tertiary thiocarbamates are easily prepared from alcohols and phenols or thiols and thiophenols by various methods, the synthesis of *N*-unsubstituted thiocarbamates is generally quite difficult [6,14–32].

The synthesis of *N*-unsubstituted (primary) *O*-thiocarbamates **1** from alcohols and phenols has been accomplished also by the following several-pot methods: The alkali salts of alcohols and

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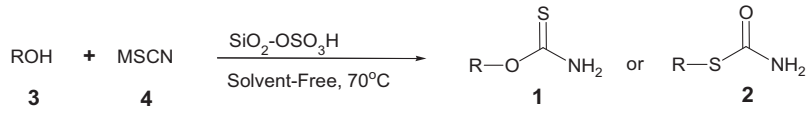


Scheme 1. Conditions of synthesis of *O*-thiocarbamates **1** and *S*-thiocarbamates **2**.

phenols react with highly toxic thiophosgene under mild conditions and form chlorothioformates which are very suitable agents for the thioacylation of ammonia [1,33,34]. They could be prepared also by reaction of cyanates with hydrogen sulfide [1,38–41]. However, alkyl or aryl cyanates must be prepared by reaction of alcohols and phenols with cyanogenbromide (BrCN); which is a highly toxic and expensive reagent [1,38–41].

There are only few reports in the literature concerning the formation of primary *S*-thiocarbamates which are carried out by hydration of organic thiocyanates in the presence of hydrogen chloride and concentrated sulfuric acid [18,29–32]. However, the preparation of alkyl or aryl thiocyanates is hindered by the same problems as mentioned for cyanates.

To the best of our knowledge, there is only one reference concerning direct addition of thiocyanic acid for the synthesis of primary *O*-ethylthiocarbamates: The yield of the reaction of ammonium thiocyanate with concentrated hydrochloric acid in ethanolic suspension is very low; it has been assumed that ethanol adds to the free thiocyanic acid [1,42].

Loev and Kormendy reported the synthesis of *N*-unsubstituted carbamates from alcohols by treatment with sodium cyanate and trifluoroacetic acid in certain organic solvents such as benzene, methylene chloride and carbon tetrachloride [43]. However, they reported when sodium thiocyanate and trifluoroacetic acid reacted with alcohols and mercaptans in attempts to extend their synthetic method to the synthesis of thiocarbamates and dithiocarbamates, they obtained only complex mixtures of odorous products.

Thermolysis of thiocarbamates resulted in a Newman and Karnes rearrangement which yields the desired *S*-arylthiocarbamates from *O*-arylthiocarbamates [20–22]. Indeed, it is a method for the transformation of phenols into thiophenols. However, these rearrangements are extremely limited [1,20–22] to useful products as are *N*,*N*-disubstituted and *N*-monosubstituted *S*-thiocarbamates.

Recently, Wynne and coworkers reported a two-step synthesis for a variety of *S*-alkyl thiocarbamates (primary, secondary and tertiary) from the reaction of thiols with trichloroacetyl chloride followed by the displacement of the trichloroacetyl group upon treatment with an amine. This procedure has the advantage of avoiding the use of phosgene entirely [14].

Since the catalytic applications of solid-state supported reagents for organic synthesis have been well established, many examples are reported on the use of silica sulfuric acid (SiO_2—OSO_3H, **SSA**) as solid acid [36,37]. **SSA** has received considerable attention as an inexpensive, non-toxic and recyclable catalyst for various organic transformations, affording the corresponding products in excellent yields with high selectivity. However, to the best of our knowledge there has been no report on the use of **SSA** for the synthesis of *O*- and *S*-thiocarbamates. Furthermore, the literature, so far published, contains neither reports about the one-pot synthesis nor the X-ray structure elucidation of primary *O*- and *S*-thiocarbamates.

In connection with the mild synthesis of primary thiocarbamates from phenols and alcohols, as we recently reported for the synthesis of carbamates [37], in this work, a simple, efficient and eco-friendly green methodology for preparation primary *S*- and *O*-thiocarbamates **1** and **2** will be introduced (Scheme 1). The idea was to provide a library of primary thiocarbamates by means of commercially available reagents in a single straightforward, simple reaction by employing non-toxic materials and preferably nongaseous reagents.

2. Results and discussion

SSA was obtained from silica gel and chlorosulfonic acid as described previously [36,37]. The primary thiocarbamates **1** and **2** were synthesized by reaction of an alcohol or phenol **3** with potassium thiocyanate **4** (M = K) in presence of SiO_2—OSO_3H at 70 °C for 12 h in moderate yields. Schematic reaction is given in Scheme 1 and the results are summarized in Table 1.

The products **1a-g** and **2a-b** were purified by column chromatography and characterized by comparing physical properties of the products with those of authentic samples [1,3,29,32,41,44]. In addition, they were characterized by ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), FT-IR, CHNS, HRMS and X-ray. The signals of NH_2 protons in ^{1}H NMR spectra are broad and split into a doublet at about δ 6–8 ppm in **1** or a singlet in **2**. The signals of the carbonyl carbon of the *O*-thiocarbamates **1** appear in ^{13}C NMR spectra at about δ 191–194 ppm (—CS—O—) and those of the *S*-thiocarbamates **2** at about δ 169 ppm (—CO—S—). Both **1** and **2** show IR vibrations at 3300 and 3400 cm^{-1} for NH_2, at 1644 cm^{-1} for the carbonyl group (—CO—S—) in **2** and at 1500–1620 cm^{-1} for the thiocarbonyl group (—CS—O—) in **1**.

The crystal structure of **1c** and **2b** were determined by X-ray diffraction methods (see Figs. 1 and 2 and Tables 2–4 for selected structural parameters). X-ray data of compounds **1c** and **2b** revealed that the nitrogen atom of NH_2 is flattened to be trigonal planar due to conjugation with the C=O or C=S groups (θ = <H1A-N1-H1B + <H1A-N1-C + <H1B-N1-C = 359°) [45,46] and coplanar with the thiocarbamate moiety adopting hereby a considerable double-bond character of the C—N bond.

Table 1
Preparation of primary *O*-thiocarbamates **1a-g** and primary *S*-alkylthiocarbamates **2a-b**.

Entry	Compound containing hydroxyl group	R	%Yield (#)	Mp (°C)	Mp (°C, Ref.)
1	**3a**	C_6H_5	36 (**1a**)	130–132	134 [1]
2	**3b**	2-$CH_3C_6H_4$	39 (**1b**)	132–134	–
3	**3c**	4-$CH_3C_6H_4$	45 (**1c**)	147–148	153 [1,40]
4	**3d**	2—$C(CH_3)_3$—4—$CH_3C_6H_3$	35 (**1d**)	166–167	–
5	**3e**	CH_3	40 (**1e**)	35–36	39–41 [1]
6	**3f**	$CH_3CH_2CH_2CH_2$	41 (**1f**)	18–19	19–21 [1]
7	**3g**	$CH_3CH_2CHCH_3$	39 (**1g**)	38–39	39–39.5 [1,41]
8	**3h**	CH_3CH_2	46 (**2a**)	106–108	108 [29,32]
9	**3i**	$(CH_3)_2CH$	44 (**2b**)	89–91	128.5 [29,32]

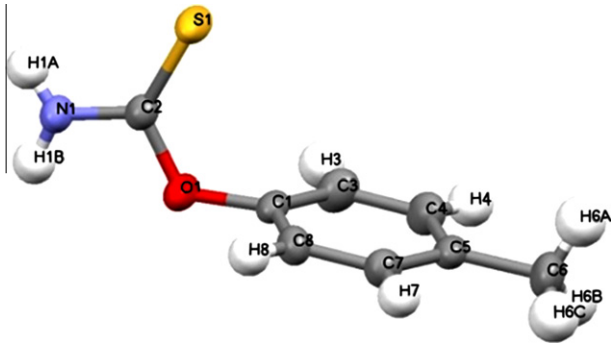


Fig. 1. X-ray structure for *O*-4-methyl–phenyl thiocarbamate **1c.**

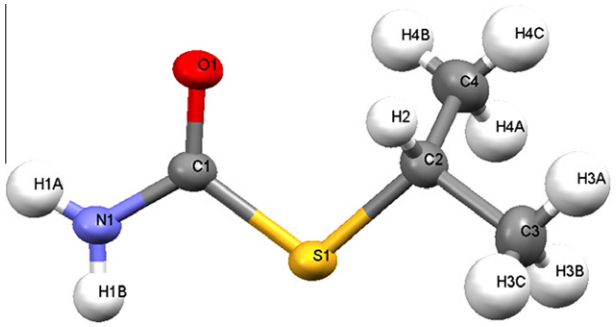


Fig. 2. X-ray structure for *S*-2-propyl thiocarbamate **2b**.

Table 2
Selected bond distances (Angstrom, Å) as obtained from the X-ray crystallographic analysis for *O*-4-methyl–phenyl thiocarbamate **1c** and *S*-2-propyl thiocarbamate **2b**.

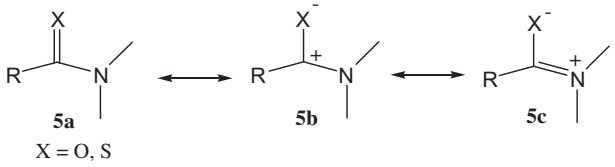
Entry	Compound	Atom1	Atom2	Length
1	**1c**	C1	O1	1.411(2)
2		C2	N1	1.314(2)
3		C2	O1	1.343(2)
4		C2	S1	1.654(2)
5		N1	H1A	0.81(2)
6		N1	H1B	0.88(2)
7	**2b**	C2	S1	1.824(1)
8		C1	N1	1.328(2)
9		C1	S1	1.778(1)
10		C1	O1	1.228(2)
11		N1	H1A	0.86(2)
12		N1	H1B	0.86(2)

Table 3
Selected bond angles (degree) as obtained from the X-ray crystallographic analysis for *O*-4-methyl–phenyl thiocarbamate **1c** and *S*-2-propyl thiocarbamate **2b**.

Entry	Compound	Atom1	Atom2	Atom3	Angle
1	**1c**	C3	C1	O1	119.3(2)
2		C8	C1	O1	118.9(2)
3		N1	C2	O1	110.0(1)
4		N1	C2	S1	125.4(1)
5		O1	C2	S1	124.6(1)
6		C2	N1	H1A	120(2)
7		C2	N1	H1B	121(1)
8		H1A	N1	H1B	118(2)
9		C1	O1	C2	120.2(1)
10	**2b**	C3	C2	S1	106.7(1)
11		C4	C2	S1	112.2(1)
12		N1	C1	S1	113.2(1)
13		N1	C1	O1	123.9(1)
14		O1	C1	S1	122.9(1)
15		C1	N1	H1A	119(1)
16		C1	N1	H1B	119(1)
17		H1A	N1	H1B	121(2)
18		C1	S1	C2	101.71(7)

Table 4
Selected torsion angles (degree) as obtained from the X-ray crystallographic analysis for *O*-4-methyl–phenyl thiocarbamate **1c** and *S*-2-propyl thiocarbamate **2b**.

Entry	Compound	Atom1	Atom2	Atom3	Atom4	Torsion
1	**1c**	C3	C1	O1	C2	−92.8(2)
2		C8	C1	O1	C2	94.3(2)
3		O1	C2	N1	H1A	−170(2)
4		O1	C2	N1	H1B	−4(1)
5		S1	C2	N1	H1A	10(2)
6		S1	C2	N1	H1B	176(1)
7		N1	C2	O1	C1	−179.4(1)
8		S1	C2	O1	C1	−0.3(2)
9	**2b**	C3	C2	S1	C1	160.3(1)
10		C4	C2	S1	C1	−76.6(1)
11		S1	C1	N1	H1A	177(2)
12		S1	C1	N1	H1B	1(1)
13		O1	C1	N1	H1A	−3(2)
14		O1	C1	N1	H1B	−179(1)
15		N1	C1	S1	C2	−175.4(1)
16		O1	C1	S1	C2	4.4(1)



Scheme 2. Canonical structures of amides/thioamides.

These planar conformational preference has been generally observed in most *N*-substituted amides, thioamides, carbamates and thiocarbamates and were rationalized in terms of negative hyperconjugation (anomeric effect) between the nitrogen lone-pair and the electron-deficient C=S or C=O bond ($\sigma^*_{C=S}$ or $\sigma^*_{C=O}$) [25,46–50].

The conformation adopted by the thiocarbamate group —OC(S)NH_2 or —SC(O)NH_2 is *syn* (C=S or C=O double bond in synperiplanar orientation with respect to the C_{aryl}—O and C_{alkyl}—O or C_{alkyl}—S single bond). Furthermore, the thiocarbamate (—O—CS—NH_2) group is oriented perpendicular to the plane of the benzene ring in **1c**.

The C—N bond in **2b** [1.329 (2) Å] in the crystaline state is longer than the same bond in **1c** [1.314 (2) Å]. Indeed, the C—N bond in **1c** seems to exhibit more double-bond character than the one in **2b**: An accepted interpretation of this feature is the higher contribution of the dipolar canonical structure **5c** (Scheme 2), because $C_{(2p)}$—$S_{(3p)}$ overlap in a thioamide bond is less effective than $C_{(2p)}$—$O_{(2p)}$ overlap in an amide bond. In other words, conjugation between the nitrogen lone pair and the thiocarbonyl group is enhanced to compensate the loss of $C_{(2p)}$—$S_{(3p)}$ overlap in **1c**. This indicates that C—N partial double bond character increases and C—N bond length subsequently decreases in carbamates in the order (*X*) O < S. This implies why the chemical shift of ^{13}C resonance of —CS—O— group in compounds **1** (191–194 ppm) is moved to higher frequency (downfield) than that in —CO—S— group in compounds **2** (169 ppm). On the other hand, the polarization of the C=S bond will be only small because electronegativities of carbon and sulfur are not much different. Thus, the contribution of the canonical structure **5b** will be significantly reduced (cf. Scheme 2). A similar behavior has been observed in thioamides compared with amides [46,51]. Moreover, the C—N bond distance in *O*-ethyl carbamate [1.349 (0.004) Å] is longer than the one in **2b** [52]. This again indicates that $C_{(2p)}$—$S_{(3p)}$ overlap in the ester group of *S*-thio-

carbamate **2b** is less effective than $C_{(2p)}$—$O_{(2p)}$ overlap in the *O*-ethylcarbamate ester group. In other words, conjugation between the nitrogen lone pair and the carbonyl group is much more reduced in *O*-ethylcarbamate relative to that in **2b**. Because one of the oxygen lone pairs on the ester group of *O*-ethylcarbamate can be donated into the carbonyl π system, and thus, it can preclude suitable π conjugation with the nitrogen lone pair.

As shown in Table 1, several primary and secondary alcohols and phenols have been used for the synthesis of primary thiocarbamates **1** and **2** employing this simple procedure.

Phenols containing electron-withdrawing substituents (CN, COOR, CHO and Br) failed to react under these experimental conditions. Most likely these functional groups decrease the nucleophilicity of the phenol oxygen for the effective attack to give the intermediate **5** and/or **7**, Scheme 3. It seems that steric hindrance of *tert*-butyl and methyl groups in comparison to hydrogen in ortho position could not affect the yield of reaction (compare entries 1, 2 and 4 in Table 1). The product of *meta*-cresol, actually, could not be characterized.

The conversions were tested using various acids such as HCl, H_2SO_4, CCl_3COOH, $HClO_4$, CF_3COOH, SiO_2—$HClO_4$, SiO_2—OSO_3H, $ClSO_3H$, $TolSO_3H$ in 13 different solvents such as H_2O, Me_2CO, Et_2O, CH_2Cl_2, $CHCl_3$, THF, n-hexane, DMSO, EtOAc, MeCN, $ClCH_2$—CH_2Cl, xylene and 1,4-dioxane. However, the formation of thiocarbamates was observed in solvents like chloroform, dichloromethane, xylene and 1,2-dichloroethylene in the presence of SiO_2—OSO_3H, CF_3COOH and $ClSO_3H$ and the best results were obtained with SiO_2—OSO_3H.

The reactions were also tested at various temperatures, times and stoichiometry ratios. The best results were obtained at the 1:1:1 stoichiometry ratio (acid, starting material and thiocyanate salt, respectively) under reflux temperature of the solvent for 24 h. Furthermore, using ammonium thiocyanate instead of potassium thiocyanate led to higher yield because of the better solubility of ammonium thiocyanate (**4**, M = NH_4).

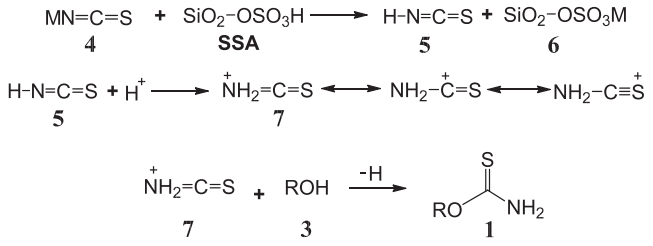
In solid-state, similar to solution, various conditions were tested; the best results were obtained for similar stoichiometric ratios 1:1:1 when reacting alcohols or phenols **3** with potassium thiocyanate **4** in the presence of SiO_2—OSO_3H at 70 °C for 12 h; moderate yields were obtained (cf. Table 1 and Scheme 1). However, in contrast to the results obtained in solution, higher yields were obtained when using potassium thiocyanate.

The most probable reaction mechanism is given in Scheme 3 and proves to be in agreement with the reaction mechanism of carbamates, published recently [37]. The reaction of potassium thiocyanate **4** (M = K) with an acid (**SSA**) to produce isothiocyanic acid **5** should be the first step [53]. Next, for the generation of the intermediate **7** (*N*-protonation is favored [53]), the proton of **SSA** is added to isothiocyanic acid **5** where it should be added to nitrogen rather than sulfur. Finally, the thiocarbamate **1** is expected to be formed when either the alcohol or phenol **2** attacks the carbon atom of intermediate **7**, Scheme 3.

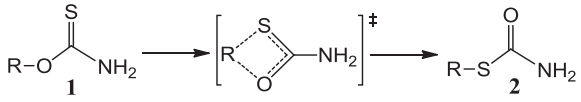
Surprisingly, we did not find products of primary *O*-thiocarbamates **1** in the case of ethanol and isopropanol. Isolation and purification yielded primary *S*-alkylthiocarbamates **2a** and **2b**, respectively. This was, in sharp contrast to the results obtained with **3a-g**. The mechanism for this transformation is not completely understood. However, based on the forgoing results, the following two mechanisms is proposed for the reaction as depicted in Schemes 4 and 5. According to the proposed mechanism, the tautomeric Miyazaki–Newman–Kwart (MNK) rearrangement can occur through a four-membered ring transition state for the formation of primary *S*-alkylthiocarbamates **2a** and **2b**, Scheme 4 [20–22]. There have been earlier reports of similar conversion of *O*-thiocarbamates to the corresponding *S*-thiocarbamates brought about by boron trifluoride-etherate or *p*-toluenesulfonic acid [54,55]; but the yields have not been mentioned. A better yield was achieved when a catalytic amount of concentrated sulfuric acid was used in chloroform solution [55].

The sulfuric acid catalyzed isomerisation was found to be quite general. The reason for the high efficiency of the sulfuric acid catalyzed process is not completely clear [55]. Therefore, similar reactions can occur with ethanol and isopropyl alcohol in the present of **SSA**.

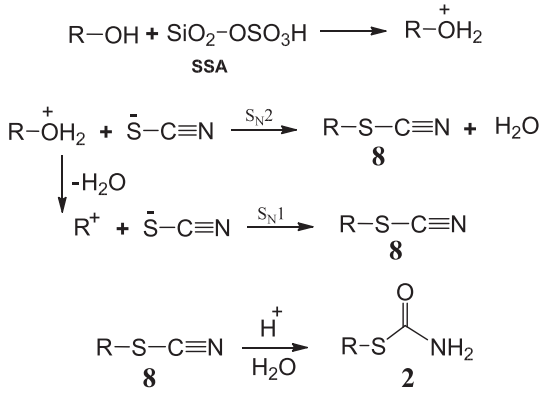
Alternatively, a proton-transfer process leads to the formation of a protonated alcohol or carbocation intermediate (ion-pair intermediate), Scheme 5. Subsequent nucleophilic attack of the thiocyanate ion to one of these intermediates via S_N1 or S_N2 should lead to alkylthiocyanate **8** and its hydrolysis to the formation of primary *S*-alkylthiocarbamates **2a** and **2b**, Scheme 5 [18,29–32]. The solid state reaction supports the stabilization of relatively unsolvated carbonium ions and can be also of value for proceeding S_N1 thiocyanations [56].



Scheme 3. Suggested mechanism of synthesis of *O*-thiocarbamates **1**.



Scheme 4. Suggested mechanism of synthesis of *S*-alkylthiocarbamates **2** via MNK rearrangement of *O*-alkylthiocarbamates **1**.



Scheme 5. Suggested mechanism of synthesis of *S*-alkylthiocarbamates **2** via thiocyanation of alcohols.

3. Conclusions

A new method to synthesize primary *O*-aryl (alkyl) thiocarbamates **1** and primary *S*-alkyl thiocarbamates **2** under mild conditions (1 atm, 70 °C without using additional base) is reported. These primary *O*- and *S*-thiocarbamates **1** and **2** could be readily prepared from cheap alcohols or phenols in a single step. Furthermore, this simple solvent-free method affords various primary thiocarbamates, with moderate yields, without involvement of toxic

solvents and expensive starting materials. Solvent-free condition, mildness of the conversion, a simple experimental procedure, clear reaction profiles and short reaction times are the noteworthy advantages of the protocol.

4. Experimental section

4.1. General

^{1}H NMR and ^{13}C NMR spectra were recorded by BRUKER AVANACE DRX500 (500 MHz). The FT-IR spectra were obtained on a JASCO FT-IR-460 plus. HRMS spectra were obtained on Q-TOF Micromass (Wakes Inc. UK). Elemental analysis was performed using Heraeus CHN-O-Rapid analyser. Melting points were recorded by Electro thermal 9100 and are uncorrected. Thin layer chromatography (TLC) was carried out using plastic sheets precoated with silica gel 60 F. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 833793 for **1c** and CCDC 833794 for **2b**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Silica sulfuric acid (**SSA**) was prepared from silica gel and chlorosulfonic acid according to the literature [36,37].

4.2. General procedure

In a typical procedure, SiO_2—OSO_3H (2 g, 1.0 mmol) was added to a mixture of potassium thiocyanate (1.0 mmol) and alcohol or phenol (1.0 mmol). Then, the mixture was heated and stirred at 70 °C in oil bath under solid-state conditions for 12 h. The reaction was monitored in TLC. After completion of reaction, ethyl acetate ($3 * 10$ ml) was added and the mixture was filtered. The solvent (EtOAc) was removed under reduced pressure and the product was purified by column chromatography (petroleum ether and ethyl acetate) and characterized correctly. Pure products were obtained in moderate yields, as summarized in Table 1.

4.3. O-Phenyl thiocarbamate

Reaction afforded white crystals **1a** (36% yield), mp = 130–132 °C ([1] 134 °C). IR (KBr); 3410 (s), 3269 (s), 3159 (s), 3016 (vw), 2957 (vw), 2925 (m), 2854 (w), 1590 (s), 1587 (vs), 1487 (s), 1421 (s), 1287 (m), 1223 (vw), 1199 (s), 1163 (vw), 1095 (w), 1025 (m), 999 (m), 910 (w), 851 (s), 772 (m), 710 (m), 690 (m), 561 (m), 507 (vw) cm^{-1}. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 6.47 (s, br, 1H, NH), 6.69 (s, br, 1H, NH), 7.12 (d, J = 7.7 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H). ^{1}H NMR (500 MHz, 293 K, acetone-d6), δppm 7.08 (d, J = 7.5 Hz, 2H), 7.24 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 8.28 (s, br, 1H, NH), 8.37 (s, br, 1H, NH). ^{13}C NMR (125 MHz, 300 K, $CDCl_3$), δppm; 122.46, 126.44, 129.31, 153.52, 191.97.

4.4. O-2-Methyl–phenyl thiocarbamate

Reaction afforded white crystals **1b** (39% yield), mp = 132–134 °C. IR (KBr); 3406 (s), 3267 (m), 3162 (m), 1597 (vs), 1489 (m), 1424 (s), 1287 (m), 1227 (m), 1177 (vs), 1113 (s), 1040 (m), 1016 (s), 856 (m), 786 (w), 774 (m), 719 (m), 569 (w), 472 (w), 418 (w) cm^{-1}. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 2.25, (s, 3H), 6.49 (s, br, 1H, NH), 6.87 (s, br, 1H, NH), 7.04 (d, J = 7.7 Hz, 1H), 7.21–7.27 (m, 3H). ^{1}H NMR (500 MHz, 298 K, acetone-d6), δppm; 2.18, (s, 3H), 6.98 (dd, J = 7.8 Hz, J = 1.1 Hz, 1H), 7.14 (dt, J = 7.5 Hz, J = 1.3 Hz, 1H), 7.18 (dt, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.23 (d, J = 7.5, 2H), 8.23 (s, br, 1H, NH), 8.32 (s, br, 1H, NH). ^{13}C NMR (125 MHz, 300 K, $CDCl_3$), δppm; 16.01, 122.61, 126.58, 126.85, 130.96, 131.16, 151.95, 191.39.

4.5. O-4-Methyl–phenyl thiocarbamate

Reaction afforded white crystals **1c** (45% yield), mp = 147–148 °C ([1,40] 153 °C). IR (KBr); 3412 (s), 3270 (m), 3158 (m), 1601 (s), 1503 (s), 1419 (s), 1291 (m), 1219 (m), 1190 (s), 1162 (m), 1104 (w), 1016 (s), 864 (m), 817 (w), 782 (vw), 713 (vw), 541 (w), 496 (w), 450 (vw) cm^{-1}. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 2.39 (s, 3H), 6.46 (s, br, 1H, NH), 6.73 (s, br, 1H, NH), 7.02 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H). ^{1}H NMR (500 MHz, 293 K, acetone-d6), δppm; 2.32 (s, 3H), 6.94 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 8.21 (s, br, 1H, NH), 8.31 (s, br, 1H, NH). ^{1}H NMR (500 MHz, 293 K, CD_3CN), δppm; 2.35 (s, 3H), 6.96 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.31 (s, br, 1H, NH), 7.44 (s, br, 1H, NH). ^{1}H NMR (300 MHz, 298 K, DMSO), δppm; 2.30 (s, 3H), 6.92 (d, J = 9.0 Hz, 2H), 7.17 (d, J = 9.0 Hz, 2H), 8.97 (s, br, 1H, NH), 9.17 (s, br, 1H, NH).^{13}C NMR (125 MHz, 300 K, $CDCl_3$), δppm; 20.95, 122.05, 129.87, 136.17, 151.30, 192.23. ^{13}C NMR (125 MHz, 300 K, acetone-d6), δppm; 20.75, 123.15, 130.14, 135.88, 152.45, 192.77. HRMS Calcd. m/z 168.0483 $[(M + 1)]^+$, Found 168.0485 $[(M + 1)]^+$. Anal. Calcd. for C_8H_9NOS: C, 57.46; H, 5.42; N, 8.38; S, 19.70, Found: C, 57.63; H, 5.26; N, 8.28, S, 19.70.

4.6. O-2-tert-butyl-4-methylphenyl thiocarbamate

Reaction afforded white crystals **1d** (35% yield), mp = 166–167 °C. IR (KBr); 3396 (m), 3282 (m), 3177 (s), 2958 (m), 2924 (m), 2857 (w), 1613 (vs), 1508 (vw), 1475 (w), 1422 (s), 1366 (w), 1288 (w), 1204 (s), 1092 (m), 1022 (m), 966 (vw), 913 (vw), 877 (vw), 847 (m), 814 (vw), 757 (w), 682 (w), 576 (w), 526 (w), 457 (vw), 418 (vw) cm^{-1}. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 1.39 (s, 9H), 2.38 (s, 3H), 6.48 (s, br, 1H, NH), 6.93 (s, br, 1H, NH), 7.00 (d, J = 8.7 Hz, 1H), 7.08 (d, J = 8.7 Hz, 1H), 7.23 (s, 1H). ^{1}H NMR (500 MHz, 293 K, acetone-d6), δppm; 1.34 (s, 9H), 2.30 (s, 3H), 6.92 (d, J = 7.9 Hz, 1H), 7.01 (d, J = 7.9 Hz, 1H), 7.19 (s, 1H), 8.29 (s, br, 2H, NH). ^{1}H NMR (500 MHz, 293 K, CD_3CN), δppm; 1.33 (s, 9H), 2.33 (s, 3H), 6.92 (d, J = 8.2 Hz, 1H), 7.03 (dd, J = 8.2 Hz, J = 2.2 Hz, 1H), 7.23 (d, J = 2.2 Hz, 1H), 7.43 (s, br, 2H, NH_2)). ^{13}C NMR (125 MHz, 300 K, $CDCl_3$), δppm; 21.31, 30.49, 34.50, 124.73, 127.18, 128.07, 135.81, 140.92, 149.67, 191.93. ^{13}C NMR (125 MHz, 300 K, acetone-d6), δppm; 21.12, 30.80, 34.96, 126.13, 127.51, 128.18, 135.49, 141.65, 150.91, 192.72. HRMS Calcd. m/z 224.1109 $[(M + 1)]^+$, Found 224.1107 $[(M + 1)]^+$. Anal. Calcd. for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67; N, 6.27; S, 14.36, Found: C, 63.98; H, 7.62; N, 6.10; S, 13.70.

4.7. O-Methyl thiocarbamate

Reaction afforded white crystals **1e** (40% yield), mp = 35–36 °C ([1] 39–41 °C). IR (KBr); 3385 (w), 3300 (m), 3250 (m), 2952 (w), 2853 (w), 1621 (vs), 1509 (w), 1438 (s), 1304 (s), 1179 (vw), 1106 (s), 943 (m), 713 (w), 419 (w) cm^{-1}. ^{1}H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 3.97 (s, 3H), 6.26 (s, br, 1H, NH), 7.00 (s, br, 1H, NH). ^{1}H NMR (500 MHz, 293 K, acetone-d6), δppm; 3.88 (s, 3H), 7.65 (s, br, 1H, NH), 7.90 (s, br, 1H, NH). ^{13}C NMR (125 MHz, 300 K, $CDCl_3$), δppm; 58.15, 193.45. HRMS Calcd. m/z 92.0170 $[(M + 1)]^+$, Found 92.0172 $[(M + 1)]^+$. Anal. Calcd. for C_2H_5NOS: C, 26.36; H, 5.53; N, 15.37; S, 35.19, Found: C, 26.51; H, 5.60; N, 15.12; S, 33.80.

4.8. O-1-Buthyl thiocarbamate

Reaction afforded white crystals **1f** (41% yield), mp = 18–19 °C ([1] 19–21 °C). IR (KBr); 3400 (m), 3289 (vs), 3171 (s), 2960 (vs), 2933 (m), 2872 (m), 1604 (vs), 1508 (vw), 1458 (m), 1409 (s), 1378 (s), 1308 (vs), 1092 (vs), 1011 (vw), 944 (w), 901 (vw), 856 (w), 738 (vw), 705 (vw), 472 (vw), 419 (vw) cm^{-1}. ^1H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 0.93 (t, J = 7.4 Hz, 3H), 1.39 (m, 2H), 1.68 (m, 2H), 4.39 (t, J = 6.7 Hz, 2H), 6.11 (s, br, 1H, NH), 6.78 (s, br, 1H, NH). ^1H NMR (500 MHz, 293 K, acetone-d6), δppm; 0.91 (t, J = 7.4 Hz, 3H), 1.38 (m, 2H), 1.64 (m, 2H), 4.34 (t, J = 6.6 Hz, 2H), 7.62 (s, br, 1H, NH), 7.84 (s, br, 1H, NH). ^{13}C NMR (125 MHz, 300 K, acetone-d6), δppm; 13.92, 19.62, 31.42, 70.92, 193.74.

4.9. O-2-Buthyl thiocarbamate

Reaction afforded white crystals **1g** (39% yield), mp = 38–39 °C ([1,41] 39–39.5 °C). IR (KBr); 3303 (vs), 3174 (s), 2970 (s), 2929 (s), 2877 (w), 1664 (s), 1601 (s), 1456 (w), 1379 (m), 1310 (s), 1175 (w), 1079 (vs), 966 (w), 896 (w), 846 (w), 789 (w), 693 (w), 490 (w) cm^{-1}. ^1H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 0.94 (t, J = 7.5 Hz, 3H), 1.31 (d, J = 6.3 Hz, 3H), 1.58–1.78 (m, 2H), 5.32 (m, 1H), 6.4 (s, br, 1H, NH), 6.61 (s, br, 1H, NH). ^1H NMR (500 MHz, 293 K, acetone-d6), δppm; 0.89 (t, J = 7.5 Hz, 3H), 1.21 (d, J = 6.3 Hz, 3H), 1.58–1.66 (m, 2H), 5.28 (m, 1H), 7.50 (s, br, 1H, NH), 7.72 (s, br, 1H, NH). ^{13}C NMR (125 MHz, 300 K, acetone-d6), δppm; 9.78, 19.39, 29.35, 78.99, 193.16.

4.10. S-Ethyl thiocarbamate

Reaction afforded white crystals **2a** (46% yield), mp = 106–108 °C ([29,32] 108 °C). IR (KBr); 3381 (s), 3219 (m), 3182 (m), 2970 (w), 2929 (w), 1644 (vs), 1617 (m), 1313 (m), 1255 (m), 1115 (w), 978 (vw), 823 (vw), 715 (m), 578 (w) cm^{-1}. ^1H NMR (500 MHz, 293 K, $CDCl_3$), δppm; 1.29, (t, J = 7.4 Hz, 3H), 2.89 (q, J = 7.4 Hz, 2H), 5.84 (s, br, 2H, NH). ^1H NMR (500 MHz, 293 K, acetone-d6), δppm; 1.21, (t, J = 7.4 Hz, 3H), 2.79 (q, J = 7.4 Hz, 2H), 6.80 (s, br, 2H, NH). ^1H NMR (500 MHz, 293 K, CD_3CN), δppm; 1.22 (t, J = 7.4 Hz, 3H), 2.80 (q, J = 7.4 Hz, 2H), 6.03 (s, br, 2H, NH). ^{13}C NMR (125 MHz, 300 K, $CDCl_3$), δppm; 15.48, 24.46, 169.85. HRMS Calcd. m/z 106.0327 $[(M + 1)]^+$, Found 106.0325 $[(M + 1)]^+$. Anal. Calcd. for C_3H_7NOS: C, 34.26; H, 6.71; N, 13.32; S, 30.49, Found: C, 34.35; H, 6.81; N, 13.37; S, 30.24.

4.11. S-2-Propyl thiocarbamate

Reaction afforded white crystals **2b** (44% yield), mp = 89–91 °C ([29,32] 128.5 °C). IR (KBr); 3370 (vs), 3281 (s), 3215 (s), 3176 (s), 2985 (m), 2965 (s), 2926 (m), 2862 (w), 2757 (w), 1644 (vs), 1614 (vs), 1462 (vw), 1441 (m), 1367 (m), 1301 (s), 1238 (s), 1156 (m), 1117 (m), 1057 (m), 931 (vw), 883 (vw), 758 (vw), 711 (s), 654 (w), 570 (m), 472 (vw), 426 (m) cm^{-1}. ^1H NMR (500 MHz, 273 K, $CDCl_3$), δppm; 1.31 (d, J = 6.9 Hz, 6H), 3.56 (h, J = 6.9 Hz, 1H), 5.54 (s, br, 2H, NH). ^1H NMR (500 MHz, 293 K, acetone-d6), δppm; 1.28 (d, J = 6.9 Hz, 6H), 3.49 (h, J = 6.9 Hz, 1H), 6.71 (s, br, 2H, NH). ^1H NMR (500 MHz, 293 K, CD_3CN) δppm; 1.29 (d, J = 6.9 Hz, 6H), 3.48 (h, J = 6.9 Hz, 1H), 6.01 (s, br, 2H, NH).^{13}C NMR (125 MHz, 300 K, acetone-d6), δppm; 23.94, 35.71, 168.53. HRMS Calcd. m/z 120.0483 $[(M + 1)]^+$, Found 120.0490 $[(M + 1)]^+$. Anal. Calcd. for C_4H_9NOS: C, 40.31; H, 7.61; N, 11.75; S, 26.90, Found: C, 40.37; H, 7.78; N, 11.71; S, 26.55.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.05.033.

Supplementary data [FT-IR, ^1H and ^{13}C NMR spectra (500 and 125 MHz) of thiocarbamates in different solvents and X-ray and HRMS data] associated with this article can be found in the online version.

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