A Facile, Safe and Inexpensive Preparation of *S*-Methyl Arylcarbamothioates by Methylthiocarbonylation of Primary Arylamines with *O*,*S*-Dimethyl Carbonodithioate

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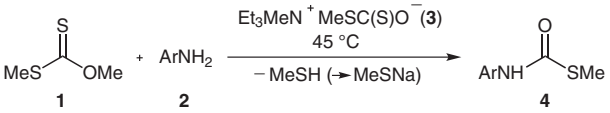
Abstract: *O*,*S*-Dimethyl carbonodithioate is proposed as a suitable and safely handled reagent that can be used in the methylthiocarbonylation of primary arylamines to give *S*-methyl arylcarbamothioates. Optimal conditions involved a one-step procedure that was carried out at 45 °C in a solvent-free system, in the presence of triethyl(methyl)ammonium *S*-methyl carbonodithioate as a reaction promoter. The title products were obtained pure in yields that, with one exception, varied between 72 and 91% (average yield of the 12 considered examples was 83%). The by-product *S*,*S*-dimethyl carbonodithioate is also a valuable reagent.

Key words: *O*,*S*-dimethyl carbonodithioate, arylcarbamothioates, thiocarbonylation, *S*,*S*-dimethyl carbonodithioate, toluene-2,4-dithiocarbamic acid *S*,*S*-dimethyl ester

S-Methyl arylcarbamothioates **4** are part of an important class of compounds, the carbamothioates (or thiocarbamates), which are of notable interest in various fields of 'fine chemicals' (especially agrochemicals and pharmaceuticals), and as starting and intermediate materials in organic synthesis.[2,3] Indeed, with regard to *S*-methyl arylcarbamothioates **4**, it has been highlighted that some can act as herbicides and parasiticides[4a] or are effective in inhibiting germination of barnyard grass seeds,[4c] are acaricides[4b] or can increase the selectivity of important carbamothioate herbicides.[4d,e] Furthermore, some of the compounds of type **4** exhibit potent inhibitory effects on the dopa oxidase activity of mushroom tyrosinase[5] or show superoxide anion-scavenging activity.[6] In the field of organic synthesis, they have been proposed as intermediates for the production of carbamates,[7] ureas,[7] and isocyanates.[8] In scientific and patent literature, also in the most recent publications, a great variety of procedures have been proposed for the preparation of *S*-alkyl arylcarbamothioates[2,4e,5,9] and, especially, of *S*-methyl arylcarbamothioates **4**. With regard to the synthesis of the latter, nearly all the procedures reported to date start with primary arylamines or their synthetic derivatives (aryl isocyanates and aryl isothiocyanates), the exception being one procedure that uses aromatic nitroderivatives as starting material. In this latter case, *S*-methyl arylcarbamothioates **4** were prepared by reductive carbonylation of aromatic nitro-derivatives with carbon monoxide in the presence of methanethiol and a catalytic system (H_2S, Et_3N, and NH_4VO_3).[10] The direct conversion of arylamines into *S*-methyl arylcarbamothioates employ the following reactions: (i) reaction, under pressure, of primary arylamines with carbon monoxide and dimethyl disulfide, catalyzed by elemental selenium[11a] or a metal selenide,[11b] in the presence of a tertiary amine; (ii) reaction of arylamines with carbon monoxide and elemental sulfur in the presence of a tertiary amine and selenium as catalyst, followed by methylation with methyl iodide;[9c,h,11c] (iii) reaction of arylamines with carbon monoxide and methanethiol in the presence of an organic base and selenium as catalyst;[9p] and (iv) reaction of arylamines with *S*-methyl chlorothioformate.[12] For the preparation of the *S*-methyl arylcarbamothioates based on the use of arylamine derivatives, the procedures are: (i) reaction of aryl isocyanates with LiAlHSH[9g] followed by methylation with methyl iodide;[5,6,9g] (ii) reaction of aryl isocyanates with dimethyl disulfide in the presence of $Zn/AlCl_3$;[9j] (iii) reaction of aryl isocyanates with methanethiol in the presence of triethylamine;[4a] (iv) reaction of aryl isothiocyanates with 3-(aminomethyl)pyridine followed by treatment of the *N*-aryl *N*′-(3-pyridylmethyl)thioureas obtained with methyl iodide;[4c] and (v) isomerization of *O*-methyl arylcarbamothioates promoted by Br_2, MeI or BF_3/Et_2O.[13] All these procedures are relatively difficult, especially if they are to be applied on a large scale, in that they are very laborious and/or start from reagents that are hazardous and/or expensive, and use costly catalysts.

The present research is aimed at the preparation of *S*-methyl arylcarbamothioates **4** by reaction of *O*,*S*-dimethyl carbonodithioate (**1**) with primary arylamines **2** in the presence of the promoter triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**; Scheme 1).



Scheme 1 Synthesis of *S*-methyl arylcarbamothioates **4a–l** by reaction of arylamines **2** with *O*,*S*-dimethyl carbonodithioate (**1**)

The study forms part of a wide ranging project that addresses the development of new, safe, and soft synthetic methodologies, based on the use of *S*,*S*-dimethyl carbonodithioate [**5**; $(MeS_2)CO$] and *O*,*S*-dimethyl carbon-

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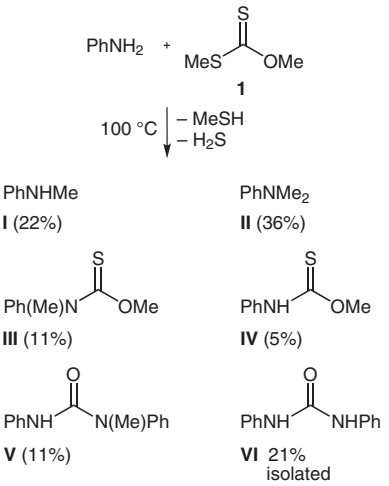
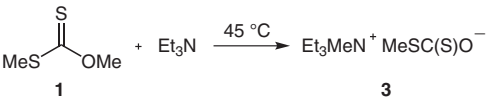
odithioate (**1**). The early research in this work addressed the use of *S*,*S*-dimethyl carbonodithioate (**5**), which is a safe and easily handled carbonylating agent that can be used as a phosgene[14] substitute for the production of various classes of compounds; specifically *S*-methyl carbamothioates,[3] carbamates,[15] and mono-, di- and trisubstituted ureas.[16] Following this, the most recent work was devoted to studying the synthetic potential of *O*,*S*-dimethyl carbonodithioate (**1**) as a substitute for *S*,*S*-dimethyl carbonodithioate (**5**), of which it is the precursor,[17] as a substitute for phosgene. This latest research has, in particular, been concerned with setting up new synthetic sequences that use reagent **1** as the starting material to prepare *S*-methyl alkylcarbamothioates and *S*-methyl dialkylcarbamothioates[18] (which, in turn, are useful as precursors of carbamates and ureas), as an alternative to the well-known synthetic sequence: *O*,*S*-dimethyl carbonodithioate (**1**) → *S*,*S*-dimethyl carbonodithioate (**5**) → *S*-methyl carbamothioates → carbamates or ureas.[3,15,18]

Achieving the objective of the present research – setting up new procedures for the synthesis of *S*-methyl arylcarbamothioates **4** based on the use of *O*,*S*-dimethyl carbonodithioate (**1**) – called for the preliminary consideration of two important experimental data reported in the literature.[19,20] One[19] concerns the impossibility of obtaining the *S*-methyl phenylcarbamothioate (**4a**) by reacting aniline with *S*,*S*-dimethyl carbonodithioate (**5**). This result, which was also confirmed in the present study, led us to exclude the use of reagent **5** for the synthesis of *S*-methyl arylcarbamothioates **4**, and prompted us to evaluate the exclusive use of *O*,*S*-dimethyl carbonodithioate (**1**). Nevertheless, this second option was counteracted by the second set of literature data[20] that established the impossibility of stopping the reaction of aniline with **1** at the *O*-methyl phenylcarbamothioate substitution product [which is useful for the conversion into its isomer *S*-methyl phenylcarbamothioate (**4a**)]. Indeed, it has been reported that this reaction proceeds until the *N*,*N*′-diphenylurea formed. In the present study we only partially confirmed this result, and found the cited reaction to be quite complex and not suitable from the preparative point of view. In fact, when aniline was reacted with *O*,*S*-dimethyl carbonodithioate (**1**) at 100 °C (Scheme 2), there was, from the very beginning of the reaction, a plentiful development of sulfur hydride and methanethiol, as is also reported in the literature,[20] together with the formation of a colorless solid consisting of *N*,*N*′-diphenylurea, which separated out from the oily reaction mixture. GC and GC-MS analyses of the mixture revealed the presence of a variety of products. The main constituents of the reaction mixture were, in the following order from the gas chromatograph: methylaniline (**I**), dimethylaniline (**II**), *O*-methyl methyl(phenyl)carbamothioate (**III**), *O*-methyl phenylcarbamothioate (**IV**), *N*-methyl-*N*,*N*′-diphenylurea (**V**) and *N*,*N*′-diphenylurea (**VI**). After eight hours, reagent **1** disappeared, whilst a portion of the aniline remained unchanged. After cooling, methylene chloride was added to the reaction mixture and the solid *N*,*N*′-diphenylurea (**V**) was collected by filtration in 21% yield. The organic solution contained the above products in the following percentages (by gas-chromatography): the starting aniline (11%), **I** (22%), **II** (36%), **III** (11%), **IV** (5%), and **V** (11%). Note that the expected simple substitution product, *O*-methyl phenylcarbamothioate (**IV**), was present as only 5%. Furthermore, the limited amount of residue remaining after solvent evaporation indicated that significant reagent loss had occurred.



Scheme 2 Reaction of aniline with *O*,*S*-dimethyl carbonodithioate (**1**) at 100 °C in the absence of the promoter triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**); the percentages reported in brackets were determined from GC analysis

On the other hand, in earlier research[18] we demonstrated the possibility of modifying the pathway followed by the reaction of primary and secondary aliphatic amines with *O*,*S*-dimethyl carbonodithioate (**1**), by working in the presence of methylammonium salts. Under these conditions, the reactions afforded directly, in a single preparative step, the *S*-methyl alkylcarbamothioates and dialkylcarbamothioates instead of the corresponding isomeric *O*-methyl alkylcarbamothioates and dialkylcarbamothioates, which usually form in the absence of such salts. On the basis of these results, we decided to apply our acquired knowledge to the synthesis of *S*-methyl arylcarbamothioates **4**. This led us to investigate the reactions of primary arylamines with *O*,*S*-dimethyl carbonodithioate (**1**) in the presence of an ammonium salt, namely anhydrous triethyl(methyl)ammonium carbonodithioate (**3**), which was prepared in situ by reacting equimolar amounts of the same carbonodithioate **1** with triethylamine, at 45 °C for two hours (Scheme 3).



Scheme 3 Synthesis of triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**) by reaction of *O*,*S*-dimethyl carbonodithioate (**1**) with triethylamine

As described previously,[18] the salt **3** separated out from the oily mixture as a colorless solid as soon as it formed. ^{1}H NMR analysis of the whole mixture (both solid and oil) showed the formation of the ammonium salt **3** (~17%) and *S*,*S*-dimethyl carbonodithioate (**5**; ~5.5%). The ratio **1**/**5** was ~90:10 (^{1}H NMR and GC analyses). In order to identify suitable conditions for the formation of *S*-methyl arylcarbamothioates **4**, we first examined the reaction of *O*,*S*-dimethyl carbonodithioate (**1**) and aniline in the presence of the said salt **3**, at 45 °C under various conditions (Table 1, entries 1–3; Procedures **A**–**C**). Procedures **A** and **B** were similar, differing only in the molar ratio of **1**/triethylamine/aniline, (**A**, 1.5:0.5:1 and **B**, 1.7:0.5:1). In these procedures, the aniline was added directly to the mixture containing **3**, which dissolved immediately. The new, homogeneous oily mixture was then dripped slowly into the *O*,*S*-dimethyl carbonodithioate (**1**), which was maintained at 45 °C. The reactions were exothermic and went to completion in one hour. During the course of the reaction the disappearance of **1** was accompanied by partial isomerization to *S*,*S*-dimethyl carbonodithioate (**5**). A part of the aniline (~10–13%) remained unchanged. In procedure **C**, the reagents were used in the same molar ratio as in procedure **A**, but the order of their mixing was reversed. All three procedures supplied the desired product, *S*-methyl phenylcarbamothioate (**4a**), in high yield (83–88%). The isomer *O*-methyl phenylcarbamothioate was present only in trace amounts and was, in any case, easily eliminated. It was also possible to recover the unreacted aniline (see the experimental section), as well as the co-product *S*,*S*-dimethyl carbonodithioate (**5**), which formed under all the reaction conditions. Procedure **D** was used when the arylamine was solid and only partially soluble in the mixture containing the ammonium salt **3** (Table 1; entry 12).

As an example: the solid 4-chloroaniline was finely ground and added, in one portion, to the said mixture containing **3**, maintained at 45 °C, then *O*,*S*-dimethyl carbonodithioate (**1**) was dripped slowly into it. The molar ratio 4-chloroaniline/**1**/triethylamine was 1:1.7:0.5. Upon addition of the first drops of **1**, both the ammonium salt **3** and the aniline dissolved. In this case, the reaction reached completion in one hour, and the *S*-methyl 4-chlorophenylcarbamothioate (**4g**) was obtained pure in 88% yield.

The results obtained in the above trials are fully consistent with the reaction mechanisms already hypothesized[18] for the reactions of aliphatic amines with *O*,*S*-dimethyl carbonodithioate (**1**) in the absence or presence of the triethyl(methyl)ammonium carbonodithioate (**3**). Thus, when the reagents *O*,*S*-dimethyl carbonodithioate (**1**) and aniline were heated to 100 °C in the absence of the methylammonium salt **3** (Scheme 4), formation of both *O*-methyl phenylcarbamothioate (**IV**) (path **A**) and *O*-methyl methyl(phenyl)carbamothioate (**III**) (path **D**) was observed, together with the development of methanethiol, through acylic nucleophilic substitution reactions proceeding by addition–elimination. At the same time, **1** acted as a methylating agent, first of aniline (path **B**) and then the resultant methylaniline (path **E**). Alongside the methylation products, i.e. methylaniline (**I**) and dimethylaniline (**II**), in the last two reactions there was also release of *S*-methyl carbonodithioic acid (**VII**), which was unstable and dissociated into methanethiol and carbon oxysulfide (path **C**). The carbon oxysulfide reacted with aniline to form phenylthiocarbamic acid (**VIII**; path **F**) which, in turn, gave rise to the phenyl isocyanate (**IX**; path **G**) by elimination of sulfur hydride. Finally, **IX** reacted with both aniline and *N*-methylaniline to supply *N*,*N*′-diphenylurea (**VI**; path **H**) and *N*-methyl-*N*,*N*′-diphenylurea (**V**; path **I**), respectively.

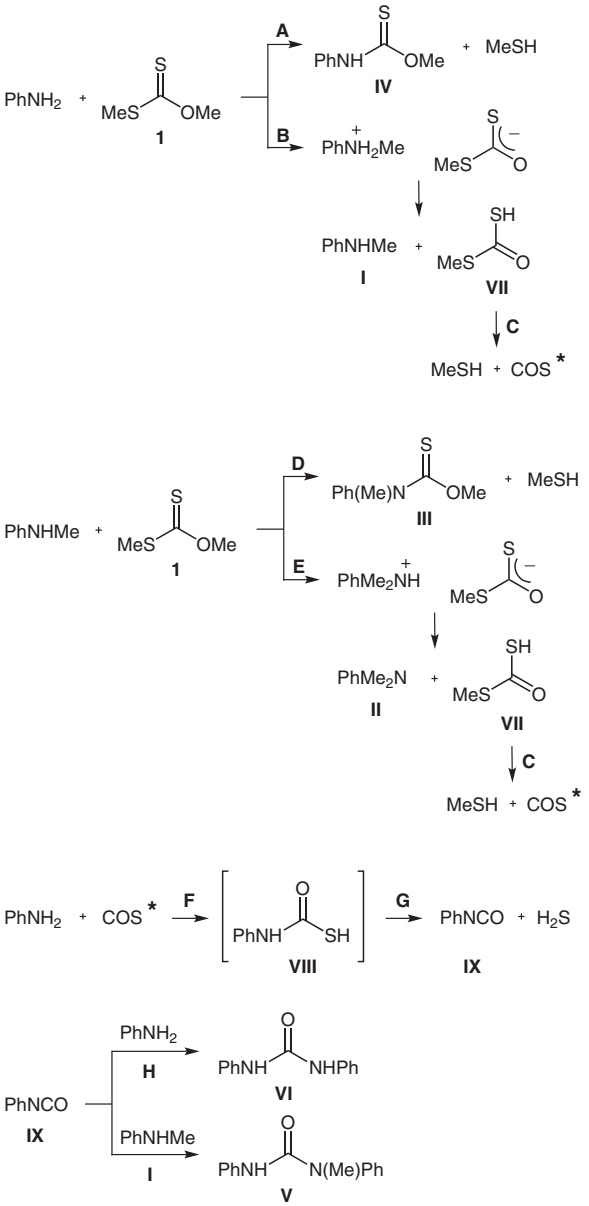
In contrast, when the reaction between *O*,*S*-dimethyl carbonothioate (**1**) and aniline was carried out in the presence of triethyl(methyl)ammonium carbonodithioate (**3**; Scheme 5), it promoted: (i) the formation of *S*-methyl phenylcarbamothioate (**4a**; paths **A** and **B**), and (ii) the isomerization of **1** to *S*,*S*-dimethyl carbonodithioate (**5**; paths **A** and **C**).

In particular, it can be hypothesized that the reaction that leads to the direct formation of *S*-methyl phenylcarbamothioate (**4a**; paths **A** and **B**) proceeds through a chain

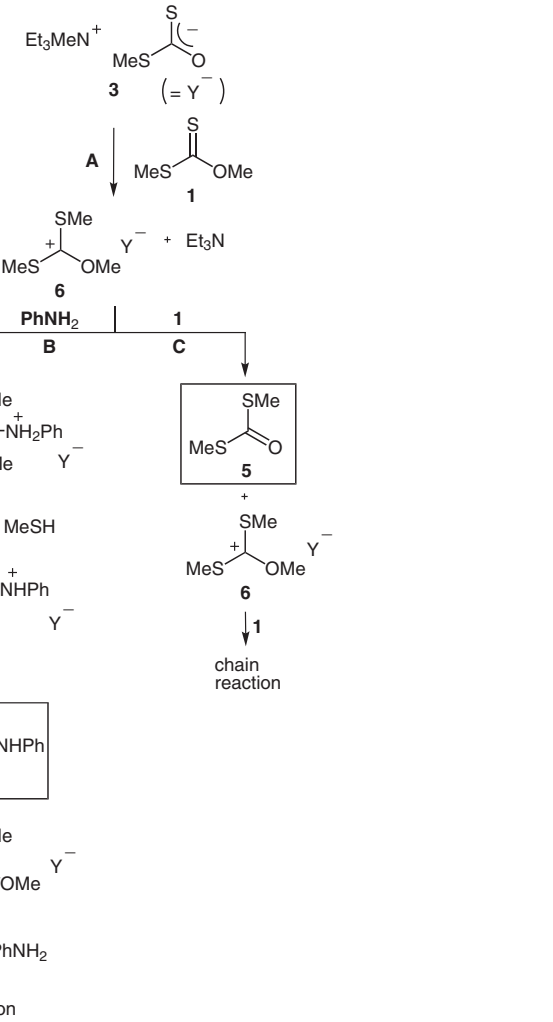
Table 1 *S*-Methyl Arylcarbamothioates **4a–l**

Entry	Ar	Procedure[a]	Molar ratio **2**/**1**/Et_3N	Compd **4**	Yield (%)[b]
1	Ph	A	1:1.5:0.5	**4a**	83
2	Ph	B	1:1.7:0.5	**4a**	88
3	Ph	C	1:1.5:0.5	**4a**	86
4	2-MeC_6H_4	A	1:1.5:0.5	**4b**	64
5	2-MeC_6H_4	B	1:1.7:0.5	**4b**	72
6	3-MeC_6H_4	A	1:1.5:0.5	**4c**	91
7	4-MeC_6H_4	A	1:1.5:0.5	**4d**	87
8	4-$MeOC_6H_4$	A	1:1.5:0.5	**4e**	90
9	4-$MeSC_6H_4$	A	1:1.5:0.5	**4f**	88
10	4-ClC_6H_4	A	1:1.5:0.5	**4g**	78
11	4-ClC_6H_4	B	1:1.7:0.5	**4g**	88
12	4-ClC_6H_4	D	1:1.7:0.5	**4g**	88
13	4-BrC_6H_4	B	1:1.7:0.5	**4h**	88
14	3-$CF_3C_6H_4$	B	1:1.7:0.5	**4i**	76
15	2,6-$Me_2C_6H_3$	A	1:1.5:0.5	**4j**	46
16	2,6-$Me_2C_6H_3$	B	1:1.7:0.5	**4j**	48
17	3,5-$Me_2C_6H_3$	A	1:1.7:0.5	**4k**	90
18	2-Me-4-(MeSCONH)C_6H_3	D	1:5.0:1	**4l**	85

[a] All the reactions were carried out at 45 °C.
[b] Yield of the pure product isolated by column chromatography (SiO_2, CH_2Cl_2).



Scheme 4 Mechanism of the reaction of aniline with *O*,*S*-dimethyl carbonodithioate (**1**) at 100 °C in the absence of the promoter triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**)



Scheme 5 Mechanism of the reaction of aniline with *O*,*S*-dimethyl carbonodithioate (**1**) at 45 °C in the presence of the promoter triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**)

reaction that is promoted by the ammonium cation of **3**. The latter can react with **1** to give the methoxybis(methylsulfanyl)methylium cation **6**, which is more prone than **1** to react with aniline (path **B**) to form the tetrahedral intermediate **7**. This intermediate then eliminates methanethiol to form the intermediate **8**, which transfers a methyl group to reagent **1**, thereby maintaining the chain reaction and giving rise to the *S*-methyl phenylcarbamothioate (**4a**). We hypothesize that path **C**, i.e. the isomerization of **1** to *S*,*S*-dimethyl carbonodithioate (**5**), can also occur through a chain reaction promoted by **3**, via **6**. In the presence of the salt **3** at the reaction temperature (~45 °C), the two reactions **B** and **C** compete with each other, but both almost exclusively prevail over other reactions that take place in the absence of the salt **3** and at higher temperature (100 °C). Evidently, the course of the reaction, in addition to being determined by the presence or absence of the promoter **3**, is also drastically influenced by the reaction temperature. On the basis of the hypothesized mechanism, one can understand why the amount of reagent **1** required by the reaction with aniline to give **4a** (Table 1, entry 2; molar ratio **1**/aniline = 1.7:1) is greater than that required by the reactions with aliphatic amines to give the *S*-methyl alkylcarbamothioates (molar ratio **1**/RNH_2 = 1:1–1.2).[18] In fact, because of the lower nucleophilicity of the aniline compared to that of the aliphatic amines, the formation of **4a** (path **B**), compared to that of the alkylcarbamothioates, is more disadvantaged, thus favoring the isomerization of **1** to **5** (path **C**).

The study was then developed further by reacting the *O*,*S*-dimethyl carbonodithioate (**1**) with substituted anilines of different nucleophilicity and steric hindrance. The considered examples show that the nucleophilicity of the anilines, which is controlled by the electronic effects of the substituents, has little influence (Table 1, entries 1–14 and 17), whereas steric hindrance has a much more

marked effect (compare: entries 2 and 3 with entries 6 and 7; entries 15 and 16 with entry 17).

Our attention then turned to a case that could have interesting implications in the field of applied chemistry: the reaction of *O*,*S*-dimethyl carbonodithioate (**1**) with toluene-2,4-diamine, carried out in the presence of triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**), prepared in situ as described above, from **1** and triethylamine (Table 1, entry 18). The reaction was performed according to procedure **D**, and required a large excess of **1** (molar ratio of amine/**1**/triethylamine, 1:5:1) and longer reaction times (2 h) to go to completion. Pure *S*,*S*-dimethyl 4-methylphenylene-1,3-di(carbamothioate) (or toluene-2,4-dithiocarbamic acid *S*,*S*-dimethyl ester) (**4l**) was easily obtained in 85% yield. Furthermore, the by-product *S*,*S*-dimethyl carbonodithioate (**5**) was isolated in a yield of 90%, calculated on the overall amount of **1** that was added to the reaction (i.e. the amounts used both to prepare the promoter **3** and for the methylthiocarbonylation of the toluene-2,4-diamine) minus the amount of **1** consumed in the reaction forming **41**. Compound **4l** has already been proposed in the literature for the synthesis of polymers.[7] In this case, it was prepared in an autoclave by reaction of toluene-2,4-diamine with carbon monoxide, dimethyl disulfide, triethylamine and elemental selenium as catalyst, in acetonitrile. This procedure, which was described in a patent,[11a] was not judged suitable for industrial applications. In contrast, we think that the procedure proposed here for the preparation of **4l** on a laboratory scale also has the requisites necessary for large-scale production; the current approach also makes **4l** a promising candidate for the production of polymers, especially polyurethanes [most likely proceeding through toluene diisocyanate (TDI)]. In this perspective it is important to highlight that the procedure is inexpensive and that, besides the low cost of the reagent *O*,*S*-dimethyl carbonodithioate (**1**) and the simple reaction conditions, the cost-effectiveness is also guaranteed by the production of methanethiol, a well known commercial reagent and, especially, of *S*,*S*-dimethyl carbonodithioate (**5**). Indeed, the latter compound is a valuable reagent that is used on both laboratory and industrial scales for thiomethylation reactions on heteroaromatic and aliphatic saturated and unsaturated substrates, with advantageous methanethiol substitution,[21] and for the production of mesyl chloride and methanesulfonic acid.[22] Furthermore, it is also used in carbonylation reactions[3,15,16] as a substitute to the extremely hazardous phosgene.[14]

In conclusion, the present research has led to the development of a new procedure that is valid for lab-scale and, potentially, large-scale syntheses of *S*-methyl arylcarbamothioates **4**. These compounds, in turn, constitute a class of starting materials that promise to be excellent for the production of isocyanates, ureas and carbamates. The procedure is based on methylthiocarbonylation of primary arylamines with *O*,*S*-dimethyl carbonodithioate (**1**) in the presence of triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**) prepared in situ by reacting **1** with triethylamine. The procedure is facile, safe and inexpensive and, were it to be applied on a large scale, it would also have the advantage of supplying the co-product *S*,*S*-dimethyl carbonodithioate (**5**), which is a valuable reagent that is industrially used in organic synthesis.

Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively. ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR spectra of samples in $CDCl_3$, unless otherwise noted, were recorded on a Bruker Avance 200 spectrometer. Mass spectra were recorded on an AT 5973N mass-selective detector connected to an AT 6890N GC, cross-linked methyl silicone capillary column. All the reactions were carried out in a solvent-free system and were performed in oven-dried glassware. No particular device was, however, adopted to exclude moisture or oxygen. Details for the reactions and yields of the pure (GC, GC-MS, ^{1}H NMR) *S*-methyl arylcarbamothioates **4** are listed in Table 1. The molecular structure of all the products were confirmed by comparison of their physical (mp or bp) and spectral data (MS, ^{1}H NMR, ^{13}C NMR) with those reported in the literature; satisfactory microanalyses were obtained for all the new compounds. The arylamines **2** were purchased from Aldrich Chemical Co and used without further purification. *O*,*S*-Dimethyl carbonodithioate (**1**) and *S*,*S*-dimethyl carbonodithioate (**5**) were supplied by Oxon Italia S.p.A. (Italy)[23] or prepared as described in the literature.[17]

S-Methyl Arylcarbamothioates 4a–l; Typical Procedures

S-Methyl Phenylcarbamothioate (4a); Procedure A (Table 1, Entry 1)

A mixture of *O*,*S*-dimethyl carbonodithioate (**1**; 1.22 g, 10 mmol) and Et_3N (1.01 g, 10 mmol) was heated to 45 °C in an oil bath, with stirring. After 10–15 min, triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**) began to form and separate from the reaction mixture as a colorless solid, according to the procedure previously reported.[18] The mixture was stirred for ~2 h. During this time the amount of solid **3** increased rapidly. ^{1}H NMR of a portion of the mixture, dissolved in $CHCl_3$, showed the presence of the starting reagents, namely **1** [δ = 2.29 (s, 3 H, SCH_3), 3.90 (s, 3 H, OCH_3); 39%] and Et_3N [δ = 0.74 (t, *J* = 7.2 Hz, 9 H, 3 × CH_2CH_3), 2.24 (q, *J* = 7.2 Hz, 6 H, 3 × CH_2CH_3); 39%], and the formed products *S*,*S*-dimethyl carbonodithioate [**5**; δ = 2.15 (s, 6 H, 2 × SCH_3); 5%] and the ammonium salt [**3**; δ = 1.15 (t, *J* = 7.3 Hz, 9 × $N^+CH_2CH_3$), 1.88 (s, 3 H, SCH_3), 2.93 (s, 3 H, N^+CH_3), 3.28 (q, *J* = 7.3 Hz, 6 H, 3 × $N^+CH_2CH_3$); similar to that reported;[18] 17%]. GC analysis of the supernatant liquid mixture, previously washed with H_2O, showed that the **1**/**5** ratio was ~90:10. After cooling to r.t., aniline (**2**; R = Ph; 1.86 g, 20 mmol) was added in one portion, with stirring. The salt **3** dissolved at once (the dissolution was endothermic), and a homogeneous liquid mixture was obtained. This new mixture was added dropwise over 6–7 min to *O*,*S*-dimethyl carbonodithioate (**1**; 2.44 g, 20 mmol), previously heated to 45 °C, with stirring (there was an immediate exothermic reaction). After 30 min, GC analysis of the oily reaction mixture showed the presence of the two starting reagents, the formation of the title compound **4a** (as the major product), and an increase in the amount of *S*,*S*-dimethyl carbonodithioate (**5**). Stirring and heating were maintained for 30 min, until the starting reagent **1** disappeared, while unreacted aniline was still present (~10–15%). MS analysis also showed traces of the following byproducts: dimethyl disulfide (*m*/*z* = 94 [M^+]), and the isomer of **4a**, i.e. *O*-methyl phenylcarbamothioate (**IV**; Scheme 4; *m*/*z* = 167 [M^+], 135 [$M^+ - CH_3OH$]). MeSH formed during the reaction was collected in aq NaOH (10–15%) and recovered as sodium methanethiolate. The mixture was treated with CH_2Cl_2–H_2O (2:1, 150 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (50 mL). The combined organic extracts were washed successively with H_2O (2 × 50 mL), aq 5% HCl (50 mL) and again with

H_2O (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The title compound **4a** was obtained pure by column chromatography (silica gel; CH_2Cl_2) of the crude residue. The byproduct *O*-methyl phenylcarbamothioate (**IV**) was also isolated in <1% yield (~0.02 g) as a colorless solid.

Yield: 2.77 g (83%, based on the aniline); colorless crystals; purity 100% (GC, MS, ^{1}H NMR).

^{1}H NMR: δ = 4.07 (s, 3 H, OCH_3), 6.85–7.38 (m, 5 H, ArH), 8.95 (br s, 1 H, NH).

MS (EI, 70 eV): *m*/*z* (%) = 167 (100) [M^+], 166 (15), 152 (4) [$M^+ - CH_3$], 151 (7), 136 (11) [$M^+ - CH_3O$], 135 [$M^+ - CH_3OH$], 134 (23), 123 (6), 119 (24), 110 (38), 109 (7), 107 (8), 106 (40), 92 (12), 91 (18), 77 (33), 75 (24), 65 (20), 51 (15).

The acidic aqueous solution was basified with aq NaOH (10%) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were repeatedly washed with H_2O (5 × 50 mL), dried (Na_2SO_4), and evaporated under reduced pressure to recover the pure unreacted aniline (GC, GC-MS, ^{1}H NMR). Yield: 0.30 g (11%).

Note: To recover the co-product *S*,*S*-dimethyl carbonodithioate (**5**), in a collateral reaction the combined organic extracts were washed and dried as above, and then slowly evaporated at atmospheric pressure, maintaining the bath temperature at 40–45 °C. The residue consisted mainly of **4a** and **5** (^{1}H NMR analysis). Column chromatography as above gave compound **5** in the first solvent fractions, which were carefully evaporated at atmospheric pressure to give a yellowish oil (1.14 g, recovery: ~70%, calculated on the overall amount of **1** that was available to react, i.e. the amounts used both for the preparation of the promoter **3** and for the methylthiocarbonylation of aniline, minus the amount of **1** consumed for the formation of **4a**). As above, the title compound **4a** was obtained in 83% yield (2.77 g).

Procedure B (Table 1, Entry 2)

The reaction was carried out according to Procedure A, with the following modification. After the reaction was stirred and heated at 45 °C for 1 h, a second portion of *O*,*S*-dimethyl carbonodithioate (**1**; 0.49 g, 4 mmol) was added dropwise over 1–2 min. After 1 h, GC analysis showed the disappearance of **1**, and a further decrease in the amount of unreacted aniline, compared with the amount present before the addition (subsequent additions of **1** were ineffective). Workup as above gave the pure title compound **4a**.

Yield: 2.94 g (88%, based on aniline).

Procedure C (Table 1, Entry 3)

The promoter triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**) was prepared as described in Procedure A and maintained at 45 °C, with stirring. A mixture of *O*,*S*-dimethyl carbonodithioate (**1**; 2.93 g, 24 mmol) and aniline (**2**, R = Ph; 1.86 g, 20 mmol) was then added dropwise over 6–7 min. The solid salt **3** dissolved at once and an exothermic reaction occurred. After the addition, stirring and heating at 45 °C were maintained for 1 h. GC analysis showed the complete disappearance of **1**, while a small amount of the unreacted aniline (8–10%, by GC analysis) was still present. Workup as above gave the pure title compound **4a**.

Yield: 2.87 g (86%, based on aniline).

***S*-Methyl 4-Bromophenylcarbamothioate (4h); Procedure B (Table 1, Entry 13)**

Finely ground 4-bromoaniline (**2**, R = 4-BrC_6H_4; 3.44 g, 20 mmol) was added in one portion to a stirred mixture containing the solid triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**), prepared as described in Procedure A by heating a mixture of *O*,*S*-dimethyl carbonodithioate (**1**; 1.22 g, 10 mmol) and Et_3N (1.01 g, 10 mmol) at 45 °C for 2 h, and then cooling to r.t. Both the solids, i.e. 4-bromoaniline and the ammonium salt **3**, dissolved (the dissolution was endothermic) and a homogeneous liquid mixture was obtained. This mixture was added dropwise over 6–7 min to *O*,*S*-dimethyl carbonodithioate (**1**; 2.44 g, 20 mmol), previously heated to 45 °C, with stirring. After 10–15 min, a solid substance began to separate from the mixture, the amount of which increased rapidly in the time. After 1 h, GC analysis showed the disappearance of **1**, while 4-bromophenylaniline was still present (~20%). A second portion of *O*,*S*-dimethyl carbonodithioate (**1**; 0.49 g, 4 mmol) was added dropwise over 1–2 min and stirring and heating were maintained for 1 h. After this time, GC analysis showed the disappearance of **1**, and a further decrease in the amount of unreacted aniline. As described in Procedure A, the reaction mixture was treated with CH_2Cl_2–H_2O (3:1, 200 mL). The aqueous solution was separated and extracted with CH_2Cl_2 (50 mL). The combined organic extracts were washed with H_2O (2 × 50 mL), aq HCl (5%, 50 mL) and again with H_2O (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The title compound **4h** was obtained pure by column chromatography (silica gel; CH_2Cl_2) of the crude residue.

Yield: 4.33 g (88%; based on 4-bromoaniline); colorless crystals; purity 100% (GC, MS, ^{1}H NMR).

***S*-Methyl 4-Chlorophenylcarbamothioate (4g); Procedure D (Table 1, Entry 12)**

Finely ground 4-chloroaniline (**2**, R = 4-ClC_6H_4; 2.55 g, 20 mmol) was directly added in one portion under stirring to a mixture containing the solid triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**), prepared as described in Procedure A by heating *O*,*S*-dimethyl carbonodithioate (**1**; 1.22 g, 10 mmol) and Et_3N (1.01 g, 10 mmol) at 45 °C for 2 h. *O*,*S*-Dimethyl carbonodithioate (**1**; 2.44 g, 20 mmol) was then added dropwise over 6–7 min. The solid ammonium salt **3** and 4-chloroaniline dissolved at once and an exothermic reaction occurred. After the addition, stirring and heating at 45 °C were maintained for 1 h. GC analysis showed the complete disappearance of **1**, while 4-chloroaniline (~20%) remained. A second portion of *O*,*S*-dimethyl carbonodithioate (**1**; 0.49 g, 4 mmol) was added dropwise over 1–2 min and stirring and heating were maintained for 1 h. After this time, GC analysis showed the disappearance of **1**, and a further decrease in the amount of unreacted 4-chloroaniline. Workup as above gave the pure title compound **4g**.

Yield: 3.54 g (88%, based on 4-chloroaniline); colorless crystals.

***S*,*S*-Dimethyl 4-Methylphenylene-1,3-di(carbamothioate) [Toluene-2,4-dithiocarbamic Acid *S*,*S*-Dimethyl Ester] (4l); Procedure D (Table 1, Entry 18)**

Finely ground toluene-2.4-diamine (1.22 g, 10 mmol) was directly added in one portion under stirring to a mixture containing the solid triethyl(methyl)ammonium *S*-methyl carbonodithioate (**3**), prepared as described in Procedure A by heating *O*,*S*-dimethyl carbonodithioate (**1**; 1.22 g, 10 mmol) and Et_3N (1.01 g, 10 mmol) at 45 °C for 2 h. *O*,*S*-Dimethyl carbonodithioate (**1**; 2.44 g, 20 mmol) was then added dropwise to the mixture over 6–7 min (when the first drops were added, an exothermic reaction occurred and the solids, i.e. salt **3** and toluene-2.4-diamine, disappeared, and a viscous brown oil formed). After 15–20 min a colorless solid began to form. During the reaction the amount of viscous brown oil decreased and, simultaneously, the amount of solid increased. GC and GC-MS analyses of the reaction mixture, carried out after 30 min, showed the disappearance of the starting reagents, i.e. **1** and toluene-2.4-diamine, and the presence of three products: *S*,*S*-dimethyl carbonodithioate (**5**; *m*/*z* = 122 [M^+], 75 [$M^+ - CH_3S$]), and toluene-2.4-diisocyanate (*m*/*z* = 174 [M^+]), as major products, and 2-aminotoluene-4-isocyanate {or 4-aminotoluene-2-isocyanate; *m*/*z* = 148 (100) [M^+], 147 (62), 120 (6), 119 (13), 106 (16), 92 (7), 65 (6)}, as a minor product. The diisocyanate and the isocyanate formed by thermal decomposition of **4l** and of the intermediate monocarbamothioate, i.e. *S*-methyl 2-aminotolyl-4-carbamothioate (or 4-aminotolyl-2-carbamothioate), respectively, under the GC conditions.

The presence of **4l** and the intermediate monocarbamothioate in the reaction mixture was confirmed by ^{1}H NMR and GC-MS analyses (for ^{1}H NMR and GC-MS data of **4l**, see below).

Monocarbamothioate

^{1}H NMR (DMSO-d_6): δ = 1.95 (s, 3 H, CH_3), 2.25 (s, 3 H, SCH_3), 4.75 (br s, 2 H, NH_2; disappeared after treatment with D_2O), 6.58 (dd, *J* = 8.1, 2.0 Hz, 1 H, ArH), 6.75 (d, *J* = 8.1 Hz, 1 H, ArH), 6.87 (d, *J* = 2.0 Hz, 1 H, ArH), 9.88 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 11.93 (SCH_3), 17.15 (CH_3), 105.26, 107.62, 116.73 (CH), 130.12, 137.73, 146.94 (C), 164.74 (C=O).

MS: *m*/*z* (%) = 196 (83) [M$^+$], 149 (20) [M$^+$ – CH_3S], 148 (100) [M$^+$ – CH_3SH], 147 (49), 121 (20), 119 (8), 106 (38), 94 (20), 93 (9), 79 (7), 77 (14).

Two further portions (each addition 1.22 g, 10 mmol) of **1** were then added after 30 and 60 min. About 30 min after each addition, GC analysis showed the disappearance of **1** and a large increase of **5**. The reaction was complete after a total time of 2 h (disappearance of the intermediate monocarbamothioate). The reaction mixture was cooled, treated with CH_2Cl_2 (100 mL), and the solid was filtered under suction on a Büchner funnel, and then was washed directly on the Büchner funnel with CH_2Cl_2 (80–100 mL). The title compound **4l** was pure by GC, GC-MS, ^{1}H NMR.

Yield: 2.30 g (85%, based on toluene-2.4-aniline); colorless solid.

^{1}H NMR of the collected organic extracts showed the presence of *S*,*S*-dimethyl carbonodithioate (**5**), as the major product, Et_3N [δ = 0.92 (t, 6 H, 3 × CH_3), 2.46 (q, 4 H, 3 × CH_2)], and the promoter triethyl(methyl)ammonium *S*-methyl carbonodithioate [**3**; δ = 1.19 (t, *J* = 7.3 Hz, 9 H, 3 × CH_2CH_3), 1.98 (s, 3 H, SCH_3), 3.00 (s, 3 H, N^+CH_3), 3.30 (q, *J* = 7.3 Hz, 6 H, 3 × CH_2); similar to that reported[18]]. The organic solution was washed with H_2O (2 × 80 mL; to remove **3**), aq HCl (5%, 50 mL; to remove Et_3N), again with H_2O (50 mL), and then dried (Na_2SO_4). The mixture was distilled at atmospheric pressure with a Vigreux distillation apparatus until the temperature of distillate was 39–40 °C (heating bath kept below 50 °C). The remaining residue was *S*,*S*-dimethyl carbonodithioate (**5**; 4.72 g; recovery: ~90%, calculated on the overall amount of **1** that was available to react, i.e. the amounts used both for the preparation of the promoter **3** and for the methylthiocarbonylation of toluene-2.4-aniline, minus the amount of **1** consumed for the formation of **4l**).

Note: In some cases, a very viscous colorless oil (instead of a solid as above) began to separate during the reaction, and the whole reaction mixture eventually became an emulsion. ^{1}H NMR analysis of the emulsion showed the presence of **4l** and *S*,*S*-dimethyl carbonodithioate (**5**), as major products, and the intermediate *S*-methyl 2-aminotolyl-4-carbamothioate (or 4-aminotolyl-2-carbamothioate), Et_3N and the promoter **3**, as minor products. The reaction reached completion with the disappearance of the intermediate monocarbamothioate. The emulsion was then allowed to cool to r.t., diluted with MeOH (10 mL), and then allowed to stand until very small colorless crystals separated. The supernatant solvent was cautiously decanted. ^{1}H NMR showed that the solid was the pure title compound **4l**. ^{1}H NMR of the liquid showed the presence of **5**, Et_3N and a small amount of **4l**.

S-Methyl Arylcarbamothioate 4a–l

Procedures and yields for *S*-methyl arylcarbamothioates **4a**–**l** are listed in Table 1; physical and spectral data, and elemental analyses for the new compounds, are reported below.

***S*-Methyl Phenylcarbamothioate (4a)**

Colorless crystals; mp 83.3–84.6 °C (CH_2Cl_2–pentane) (Lit.[9h] 84.6 °C; Lit.[6a] 71.2–72.8 °C).

^{1}H NMR: δ = 2.43 (s, 3 H, SCH_3), 7.11 (app t, *J* = 7.5 Hz, 1 H, ArH), 7.32 (br s, 1 H, NH), 7.32 (app t, *J* = 7.5 Hz, 2 H, ArH), 7.43 (app d, *J* = 7.5 Hz, 2 H, ArH). Identical to the reported spectrum.[6a]

^{13}C NMR: δ = 14.09 (CH_3), 121.40, 125.90, 130.55 (CH), 139.24 (C), 168.15 (C=O). Similar to the reported spectrum.[6a]

MS (EI, 70 eV): *m*/*z* (%) = 167 (41) [M$^+$], 120 (26) [M$^+$ – CH_3S], 119 (100) [M$^+$ – CH_3SH], 92 (26), 91 (19), 77 (27), 75 (9), 65 (15), 64 (8), 51 (6).

***S*-Methyl 2-Tolylcarbamothioate (4b)**

Colorless crystals; mp 78.3–79.5 °C (CH_2Cl_2–pentane) (Lit.[24] 70 °C). Spectral data are not reported.

^{1}H NMR: δ = 2.26 (s, 3 H, CH_3), 2.40 (s, 3 H, SCH_3), 7.07–7.27 (2 × m, partially overlapped, 4 H, ArH and NH; NH disappeared after treatment with D_2O), 7.58 (app d, *J* = 7.4 Hz, 1 H, ArH).

^{13}C NMR: δ = 14.09 (SCH_3), 19.19 (CH_3), 126.22, 127.62, 128.20, 131.59 (CH), 132.10, 136.79 (C), 169.16 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 181 (73) [M$^+$], 134 (39) [M$^+$ – CH_3S], 133 (100) [M$^+$ – CH_3SH], 132 (11), 106 (38), 105 (28), 104 (37), 91 (56), 79 (8), 78 (15), 77 (23), 75 (12), 65 (10).

***S*-Methyl 3-Tolylcarbamothioate (4c)**

The compound is known, but physical and spectral data were not reported.[4c,d]

Colorless crystals; mp 68.6–69.7 °C (CH_2Cl_2–pentane).

^{1}H NMR: δ = 2.32 (s, 3 H, CH_3), 2.43 (s, 3 H, SCH_3), 6.95 (app d, *J* = 5.4 Hz, 1 H, ArH), 7.13–7.24 (m, 2 H, ArH), 7.29 (br s, 1 H, ArH), 7.45 (br s, 1 H, NH).

^{13}C NMR: δ = 14.10 (SCH_3), 22.87 (CH_3), 118.50, 122.08, 126.71, 130.34 (CH), 139.16, 140.50 (C), 168.06 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 181 (60) [M$^+$], 134 (29) [M$^+$ – CH_3S], 133 (100) [M$^+$ – CH_3SH], 132 (15), 106 (25), 105 (7), 104 (20), 91 (42), 79 (9), 78 (10), 77 (18), 65 (8).

Anal. Calcd for $C_9H_{11}NOS$: C, 59.64; H, 6.12; N, 7.73; S, 17.69. Found: C, 59.57; H, 6.14; N, 7.71; S, 17.68.

***S*-Methyl 4-Tolylcarbamothioate (4d)**

Colorless crystals; mp 111–112 °C (CH_2Cl_2) (Lit.[6a] 102.1–103.5 °C).

^{1}H NMR: δ = 2.22 (s, 3 H, CH_3), 2.42 (s, 3 H, SCH_3), 7.12 (app d, *J* = 8.4 Hz, 2 H, ArH), 7.20 (br s, 1 H, NH; disappeared after treatment with D_2O), 7.27 (dt, *J* = 8.4, 2.4 Hz, 2 H, ArH). Similar to the reported spectrum.[6a]

^{13}C NMR: δ = 14.05 (SCH_3), 22.28 (CH_3), 121.73, 131.04 (CH), 135.71, 136.58 (C), 167.94 (C=O). Similar to the reported spectrum.[6a]

MS (EI, 70 eV): *m*/*z* (%) = 181 (65) [M$^+$], 134 (23) [M$^+$ – CH_3S], 133 (100) [M$^+$ – CH_3SH], 132 (22), 106 (53), 105 (9), 104 (21), 91 (24), 79 (10), 78 (11), 77 (20), 75 (8), 65 (7).

***S*-Methyl 4-Methoxyphenylcarbamothioate (4e)**

Colorless crystals; mp 102.1–102.8 °C (CH_2Cl_2).

^{1}H NMR: δ = 2.39 (s, 3 H, SCH_3), 3.78 (s, 3 H, OCH_3), 6.84 (dt, *J* = 9.0, 2.7 Hz, and m, partially overlapped, 3 H, 2 × ArH and NH; NH disappeared after treatment with D_2O), 7.31 (dt, *J* = 9.0, 2.7 Hz, 2 H, ArH).

^{13}C NMR: δ = 12.41 (SCH_3), 55.28 (OCH_3), 114.05, 122.13 (CH), 130.41, 156.60 (C), 166.79 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 197 (66) [M$^+$], 150 (13) [M$^+$ – CH_3S], 149 (100) [M$^+$ – CH_3SH], 134 (40), 123 (7), 122 (82), 106 (19), 95 (10), 78 (10), 75 (8), 52 (10).

Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62; N, 7.10; S, 16.26. Found: C, 54.84; H, 5.65; N, 7.10; S, 16.29.

S-Methyl 4-Methylsulfanylphenylcarbamothioate (4f)
Colorless crystals; mp 123.1–123.7 °C (CH_2Cl_2).

^{1}H NMR: δ = 2.42 (s, 3 H, SCH_3), 2.47 (s, 3 H, Ar-SCH_3), 7.22 (dt, *J* = 8.8, 2.3 Hz, 2 H, ArH), 7.27 (br s, 1 H, NH), 7.35 (dt, *J* = 8.8, 2.3 Hz, 2 H, ArH).

^{13}C NMR: δ = 12.45 (SCH_3), 16.38 (C-SCH_3), 120.40, 122.78 (CH), 133.74, 135.09 (C), 166.22 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 213 (72) [M^+], 166 (12) [$M^+ - CH_3S$], 165 (100) [$M^+ - CH_3SH$], 150 (37), 139 (6), 138 (63), 106 (9), 96 (7), 75 (8).

Anal. Calcd for $C_9H_{11}NOS_2$: C, 50.67; H, 5.20; N, 6.57; S, 30.06. Found: C, 50.78; H, 5.19; N, 6.53; S, 30.09.

S-Methyl 4-Chlorophenylcarbamothioate (4g)
Colorless crystals; mp 132.5–133.6 °C (CH_2Cl_2) (Lit.[6a] 130.5–131.5 °C).

^{1}H NMR: δ = 2.42 (s, 3 H, SCH_3), 2.47 (s, 3 H, SCH_3), 7.22 (dt, *J* = 8.8, 2.3 Hz, 2 H, ArH), 7.27 (br s, 1 H, NH), 7.35 (dt, *J* = 8.8, 2.3 Hz, 2 H, ArH). Similar to the reported spectrum.[6a]

^{13}C NMR: δ = 12.45 (SCH_3), 120.79, 128.95 (CH), 129.23, 136.10 (C), 166.33 (C=O). Similar to the reported spectrum.[6a]

MS (EI, 70 eV): *m*/*z* (%) = 201 (30) [M^+], 155 (33), 154 (16) [$M^+ - SCH_3$], 153 (100) [$M^+ - CH_3SH$], 128 (9), 127 (10), 126 (28), 125 (25), 99 (11), 90 (15), 75 (17), 63 (10).

S-Methyl 4-Bromophenylcarbamothioate (4h)
Colorless crystals; mp 145–146.2 °C (CH_2Cl_2).

^{1}H NMR: δ = 2.43 (s, 3 H, SCH_3), 7.34 (dt, *J* = 9.0, 2.4 Hz, 2 H, ArH), 7.42 (dt, *J* = 9.0, 2.4 Hz, 2 H, ArH).

^{13}C NMR: δ = 14.10 (SCH_3), 118.43, 122.71 (CH), 133.52, 138.25 (C), 168.00 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 247 (36) [M^+], 245 (34), 200 (16) [$M^+ - CH_3S$], 199 (97) [$M^+ - CH_3SH$], 198 (17), 197 (100), 172 (29), 171 (17), 170 (309), 169 (14), 91 (18), 90 (24), 75 (23), 64 (11), 63 (18).

Anal. Calcd for C_8H_8BrNOS: C, 39.04; H, 3.28; N, 5.69; S, 13.03. Found: C, 39.14; H, 3.30; N, 5.69; S, 13.04.

S-Methyl 3-Trifluoromethylphenylcarbamothioate (4i)
Colorless crystals; mp 101.4–102.8 °C (CH_2Cl_2).

^{1}H NMR: δ = 2.38 (s, 3 H, SCH_3), 7.25–7.35 (m, 2 H, ArH), 7.38 (app d, *J* = 7.7 Hz, 1 H, ArH), 7.54 (dt, *J* = 7.7, 1.6 Hz, 1 H, ArH), 7.68 (br s, 1 H, NH).

^{13}C NMR: δ = 12.43 (SCH_3), 115.07, 120.65, 126.24, 131.50 (q, J_{C-F} = 271.0 Hz, CF_3), 120.72, 121.00, 129.48 (CH), 130.39, 131.04, 131.68, 132.33 (q, J_{C-F} = 32.5 Hz, *C*CF_3), 138.04 (C), 166.64 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 235 (25) [M^+], 188 (29) [$M^+ - CH_3S$], 187 (100) [$M^+ - CH_3SH$], 160 (22), 145 (20), 140 (7), 75 (16).

Anal. Calcd for $C_9H_8F_3NOS$: C, 45.95; H, 3.43; N, 5.95; S, 13.63. Found: C, 46.02; H, 3.39; N, 5.90; S, 13.68.

S-Methyl 2,6-Dimethylphenylcarbamothioate (4j)
Colorless crystals; mp 95.7–96.3 °C (EtOAc–pentane).

^{1}H NMR ($CDCl_3$): δ = 2.23 (br s, 9 H, 2 × CH_3 and SCH_3), 6.83 (m, 1 H, ArNH; disappeared after treatment with D_2O), 7.05 (m, 3 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 12.23 (SCH_3), 18.12 (CH_3), 128.16, 132.57 (CH), 135.49, 138.01 (C), 171.73 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 195 (61) [M^+], 148 (42) [$M^+ - CH_3S$], 147 (100) [$M^+ - CH_3SH$], 146 (7), 132 (12), 120 (36), 119 (32), 118 (21), 105 (54), 92 (8), 79 (8), 77 (20), 75 (9), 65 (7).

Anal. Calcd for $C_{10}H_{13}NOS$: C, 61.50; H, 6.71; N, 7.17; S, 16.42. Found: C, 61.49; H, 6.65; N, 7.13; S, 16.49.

S-Methyl 3,5-Dimethylphenylcarbamothioate (4k)
Colorless crystals; mp 115.4–115.8 °C (CH_2Cl_2).

^{1}H NMR: δ = 2.30 (s, 6 H, 2 × CH_3), 2.43 (s, 3 H, SCH_3), 6.77 (br s, 1 H, ArH), 7.06 (br s, 2 H, ArH), 7.27 (br s, 1 H, NH).

^{13}C NMR: δ = 12.44 (SCH_3), 21.12 (CH_3), 117.48, 126.02 (CH), 137.38, 138.66 (C), 166.15 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 195 (65) [M^+], 148 (29) [$M^+ - CH_3S$], 147 (100) [$M^+ - CH_3SH$], 146 (10), 132 (31), 120 (24), 118 (10), 105 (40), 91 (15), 79 (7), 77 (18).

Anal. Calcd for $C_{10}H_{13}NOS$: C, 61.50; H, 6.71; N, 7.17; S, 16.42. Found: C, 61.62; H, 6.65; N, 7.14; S, 16.45.

S,S-Dimethyl 4-Methylphenylene-1,3-di(carbamothioate) [Toluene-2,4-dithiocarbamic Acid S,S-Dimethyl Ester] (4l)
Spectral data were not reported.

Colorless crystals; mp 195.2–196.3 °C (toluene) (Lit.[7,11a] mp 185 °C).

^{1}H NMR (DMSO-d_6): δ = 2.11 (s, 3 H, CH_3), 2.26 (s, 3 H, SCH_3), 2.28 (s, 3 H, SCH_3), 7.12 (d, *J* = 8.3 Hz, 1 H, ArH), 7.25 (dd, *J* = 8.3, 2.1 Hz, 1 H, ArH), 7.51 (d, *J* = 2.1 Hz, 1 H, ArH), 9.69 (br s, 1 H, NH), 10.27 (br s, 1 H, NH).

^{13}C NMR (DMSO-d_6): δ = 13.60 (SCH_3), 19.09 (CH_3), 118.41, 129.35 (CH), 132.44, 138.09, 138.95 (C), 167.00, 168.06 (C=O).

MS (EI, 70 eV): Under the GC-MS conditions, **4l** decomposed and three products were revealed, in the following order: (1) toluene-2,4-diisocyanate: *m*/*z* (%) = 174 (100) [M^+], 173 (26), 146 (28), 145 (62), 132 (16), 119 (8), 118 (10), 91 (11), 76 (6); (2) *S*-methyl 2-isocyanatotolyl-4-carbamothioate [or 4-isocyanatotolyl-2-carbamothioate]: *m*/*z* (%) = 222 (65) [M^+], 175 (25) [$M^+ - CH_3S$], 174 (100) [$M^+ - CH_3SH$], 173 (12), 147 (34), 146 (23), 145 (34), 132 (13), 119 (5), 118 (7), 104 (13), 92 (8), 91 (7), 77 (16), 75 (19), 65 (7); (3) *S*-methyl 4-isocyanatotolyl-2-carbamothioate [or 2-isocyanatotolyl-4-carbamothioate]: *m*/*z* (%) = 222 (55) [M^+], 207 (6), 175 (34) [$M^+ - CH_3S$], 174 (100) [$M^+ - CH_3SH$], 173 (13), 147 (29), 146 (24), 145 (35), 132 (34), 119 (5), 118 (7), 104 (5), 92 (5), 91 (6), 77 (12), 75 (19), 65 (7).

Trial Reactions

A) Reactions with Arylamines and S,S-Dimethyl Carbonodithioate (5)

1) A mixture of aniline (0.93 g, 10 mmol) and *S*,*S*-dimethyl carbonodithioate (**5**; 1.22 g, 10 mmol) was heated to 180 °C with an oil bath for 10 h, with stirring. The reaction failed; GC and GC-MS analyses of the mixture showed the presence of only unchanged starting reagents.

2) A mixture of 4-methoxyaniline (1.23 g, 10 mmol) and *S*,*S*-dimethyl carbonodithioate (**5**; 1.22 g, 10 mmol) was heated to 185 °C with an oil bath for 5 h, with stirring. The reaction failed (GC and GC-MS analyses).

3) A mixture of 4-methoxyaniline (1.23 g, 10 mmol) and *S*,*S*-dimethyl carbonodithioate (**5**; 1.22 g, 10 mmol) was dissolved in anhydrous toluene and the obtained solution was heated to reflux (111 °C) for 8 h. The reaction failed (GC and GC-MS analyses).

B) Reaction of Aniline with *O*,*S*-Dimethyl Carbonodithioate (1) in the Absence of Triethyl(methyl)ammonium *S*-Methyl Carbonodithioate (3)

1) A mixture of aniline (0.93 g, 10 mmol) and *O*,*S*-dimethyl carbonodithioate (**1**; 1.22 g, 10 mmol) was heated to 45 °C for 4 h, with stirring. GC and GC-MS analyses showed the presence of traces of *N*-methylaniline, in addition to the two unchanged reagents. When the mixture was then heated to 60 °C for 2 h, the amount of *N*-methylaniline increased (2–3%). After heating to 80 °C for 4 h, the amount of *N*-methylaniline increased to 7–8% and *N*,*N*-dimethylaniline and *N*,*N*′-diphenylurea began to form.

2) The above mixture was directly heated to 100 °C, with stirring. After 3 h, about 10% of the reagent **1** was still present and the following products were formed: *N*-methylaniline (**I**: *m*/*z* = 107 [M^+]) and *N*,*N*-dimethylaniline (**II**: *m*/*z* = 121 [M^+]), as major products, and *O*-methyl *N*-methyl-*N*-phenylcarbamothioate (**III**: *m*/*z* = 181 [M^+], 106 [$M^+ - CH_3$], 150 [$M^+ - CH_3O$]), *O*-methyl phenylcarbamothioate (**IV**: *m*/*z* = 167 [M^+], 152 [$M^+ - CH_3$], 135 [$M^+ - CH_3OH$]), *N*-methyl-*N*,*N*′-diphenylurea (**V**: *m*/*z* = 226 [M^+]) and *N*,*N*′-diphenylurea (**VI**: *m*/*z* = 212 [M^+]). A colorless solid began to separate from the reaction mixture, which increased over time together with plentiful gas evolution (MeSH and H_2S) observed. After 8 h, the starting *O*,*S*-dimethyl carbonodithioate (**1**) disappeared, while about 10% of aniline was still present. The mixture was diluted with CH_2Cl_2 (50 mL) and the solid was filtered under suction on a Büchner funnel and then washed directly on the Büchner funnel with further CH_2Cl_2 (10 mL). The colorless solid was pure (GC, GC-MS, ^1H NMR) *N*,*N*′-diphenylurea (**VI**; 0.23 g, 21%). GC and GC-MS analyses of the collected organic solutions revealed the presence of unreacted aniline and the above products, in the following GC order and percentage ratio: aniline (10%), **I** (22%), **II** (36%), **III** (11%), **IV** (5%), **V** (11%). After evaporation of the solvent under reduced pressure, 0.73 g of residue remained.

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