# An Easy and Efficient One-Step Procedure for the Preparation of Alkyl and Aryl Alkylcarbamates from *S*-Methyl *N*-Alkylthiocarbamates

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**Abstract:** A general, one-step procedure for the synthesis of alkyl and aryl alkylcarbamates, by the direct reaction of *S*-methyl *N*-alkylthiocarbamates with alcohols or phenols in toluene at reflux in the presence of triethylamine, is reported. All the target products were obtained in high yield (15 examples, average yield 94%) and very high purity (>99.2%). The recovery of a co-product of industrial interest, methanethiol, in an amount of one mole for each mole of thiocarbamate, with complete exploitation of the reagent, should also be noted.

**Key words:** carbamates, thiocarbamates, *S*,*S*-dimethyl dithiocarbonate, green chemistry

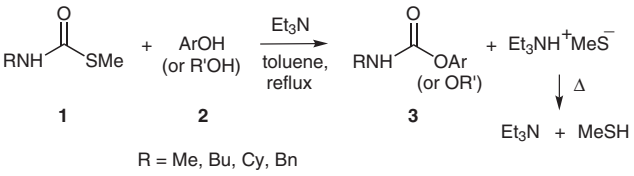
Carbamates (or urethanes) are an important class of compounds with a wide range of applications as herbicides, fungicides and pesticides in the agrochemical industry, as drugs and drug intermediates in the pharmaceutical industry, as protective groups for amine function in peptide chemistry, as starting materials (for producing isocyanates and polyurethanes), and synthetic intermediates (for producing fine and commodity chemicals) in the chemical industry, and as linkers in combinatorial chemistry.[2–4] Most classical syntheses of carbamates are based on either the direct, or indirect, utilization of toxic and harmful reagents (phosgene/isocyanates/carbon monoxide) as a source of the carbonyl.[2–4] In addition to the growing demand for environmental friendly technologies, significant effort has been put into developing procedures aimed at avoiding the use of such hazardous chemicals.

It is in this context that we recently established a new synthetic methodology that uses the non-toxic, and hazard-free *S*,*S*-dimethyl dithiocarbonate (DMDTC) as a carbonylating agent for the preparation of alkyl and aryl alkylcarbamates.[4] More precisely, we recently developed a general, low-cost, safe, and eco-friendly procedure for the selective preparation of *S*-methyl *N*-alkylthiocarbamates **1** by methylthiocarbonylation of primary aliphatic amines with DMDTC.[5] The reactions were carried out in water at room temperature, and the target products **1** were obtained in exceptionally high yield and very high purity, usually >95% and >99.5%, respectively. This procedure has the advantage of making the *S*-methyl *N*-alkylthiocarbamates readily available, also on larger scales. Following this preliminary step, the crude *S*-methyl *N*-alkylthiocarbamates **1** were used as raw materials to produce alkyl and aryl alkylcarbamates **3**, employing a procedure that involves three steps carried out in a one-pot fashion.[4] In the first step, reaction of compounds **1** with chlorine in dimethyl disulfide at –10/–15 °C led to the formation of the corresponding carbamoyl chlorides; in the second step, treatment with triethylamine at 0–5 °C converted these chlorides into the alkyl isocyanates. In the third and final step, these isocyanates were reacted with alcohols or phenols at temperatures varying between room temperature and 70 °C, forming the pure alkyl and aryl alkylcarbamates **3** in excellent yields. Indeed, the average yield of the 16 considered examples was 91% and the GC purity was greater than 99%.

The objective of the present work was to evaluate the possibility of directly converting the crude *S*-methyl *N*-alkylthiocarbamates **1**, prepared as described above,[5] into the alkyl and aryl alkylcarbamates **3**, using a one-step, rather than the previously reported[4] three-step procedure.

To the best of our knowledge, the only literature-reported work[6] related to the one-step conversion of *N*-alkylthiocarbamates into the corresponding alkylcarbamates concerns the reaction of *S*-methyl *N*-methylthiocarbamate with methanol, at 20 hours reflux in the presence of sodium, and with 1-naphthol in benzene or acetonitrile, always at 21–23 hours reflux, in the presence of zinc chloride and triethylamine, respectively. The first reaction gave methyl methylcarbamate in 85% yield, whereas the other two reactions gave 1-naphthyl methylcarbamate (carbaryl) in 50% yield. Obviously, these results were insufficient to permit an evaluation of the procedure's merits.

In the procedure presented here, the crude *S*-methyl *N*-alkylthiocarbamates **1** were reacted with alcohols or phenols **2** in anhydrous toluene, at reflux, in the presence of triethylamine (Scheme 1). Details for all the reactions, including yields, purity and physical properties of the alkyl and aryl alkylcarbamates **3a–o** are reported in Table 1.




**Scheme 1**

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**Table 1** Alkyl and Aryl Alkylcarbamates **3a–o**[a]

| Entry | R | Ar or R′ | Ratio (**2**:**1**) | Time (h) | Product | Yield (%)[b] | GC purity (%) | MS *m/z* [M$^+$] | Mp (°C) or bp (°C / mmHg) Crude | Recrystallized (solvent) | Lit. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Me | 4-Br$C_6H_4$ | 3:1 | 5 | **3a** | 87 | 100 | 230 | 119.8–121.8 | 122.9–123.3 (toluene) | 120.5–121.5[7] |
| 2 | | | 2:1 | 12 | **3a** | 83 | 99.3 | 230 | 117.6–119.9 | | |
| 3 | | | 1:1 | 24[c] | **3a** | 48[d] | 100 | 230 | 120.2–121.0 | | |
| 4 | Me | 3,5-$Me_2C_6H_3$ | 3:1 | 4 | **3b** | 87 | 99.7 | 179 | 99.9–101.4 | 101–102 (toluene–pentane) | 100.8–101.5[4] |
| 5 | | | 2:1 | 6 | **3b** | 86[e] | 100 | 179 | 100.7–101.4 | | |
| 6 | Me | 1-Naphthyl | 3:1 | 4 | **3c** | 80 | 100 | 201 | 141.7–142.5 | 143 (toluene–pentane) | 143[4] |
| 7 | | | 2:1 | 8 | **3c** | 80 | 100 | 201 | 142.1–143 | | |
| 8 | | | 1:1 | 24[c] | **3c** | 41[d] | 100 | 201 | 141.4–142.9 | | |
| 9 | Me | Bn | 3:1 | 7 | **3d** | 88[f,g] | 100 | 165 | oil | 124–125/0.6 | 118/0.5[4] |
| 10 | | | 2:1 | 12 | **3d** | 88[f,g] | 100 | 165 | oil | | |
| 11 | | | 1:1 | 24[c] | **3d** | 64[f] | 100 | 165 | oil | | |
| 12 | Bu | Me | –[h] | 22 | **3e** | 88 | 99.4 | 131 | oil | 94–95/15 | 92/15[8] |
| 13 | Bu | Bu | 2:1 | 24 | **3f** | 91 | 99.4 | 173 | oil | 138–140/15 | 88/3[9] |
| 14 | | | –[i] | 4 | **3f** | 98 | 99.9 | 173 | oil | | |
| 15 | Bu | HC≡$CCH_2$ | 2:1 | 12 | **3g** | 94 | 100 | 155 | oil | 95–96/0.6 | 90–91/0.5[4] |
| 16 | | | 1.5:1[11] | 24 | **3g** | 87[11] | 100 | 155 | oil | | |
| 17 | Bu | 4-$MeOC_6H_4$ | 2:1 | 12 | **3h** | 98 | 99.8 | 223 | 75.8–76.6 | 77.8–78.3 (toluene–pentane) | –[j] |
| 18 | Cy | 4-$ClC_6H_4$ | 2:1 | 13 | **3i** | 97 | 99.2 | 253 | 169.0–170.3 | 173.4–174.4 (toluene–pentane) | 173.7–174.7[4] |
| 19 | Bn | Bu | 2:1 | 24 | **3j** | 96 | 99.4 | 207 | oil | 192–193/35 | –[k] |
| 20 | | | –[i] | 4 | **3j** | 100 | 99.2 | 207 | oil | | |
| 21 | Bn | *n*-$C_8H_{17}$ | 2:1 | 10 | **3k** | 96[m] | 99.9 | 263 | 51.6–52.8 | 51.8–52.5 (pentane) | –[l] |
| 22 | Bn | *n*-$C_{16}H_{33}$ | 2:1 | 6 | **3l** | 99[n] | 100[o] | 375 | 81.9–83.2 | 82.3–83.2 (toluene) | |
| 23 | | | 1:1 | 24 | **3l** | 98 | 99.5[o] | 375 | 79.5–80.3 | | |
| 24 | Bn | Bn | 2:1 | 8 | **3m** | 99 | 99.9 | 241 | 64.1–64.8 | 64.9–65.6 (toluene–pentane) | 64[14] |
| 25 | | | 1:1 | 14 | **3m** | 95 | 99.7 | 241 | 63.9–64.8 | | |
| 26 | Bn | 4-Br$C_6H_4$ | 3:1 | 6 | **3n** | 96 | 100 | 306 | 167.7–168.7 | 168.3–169.4 ($CHCl_3$) | 167.9–168.8[4] |
| 27 | | | 2:1 | 7 | **3n** | 96 | 100 | 306 | 168.2–169.4 | | |
| 28 | | | 1:1 | 20 | **3n** | 95 | 99.6 | 306 | 168.3–169.4 | | |

**Table 1** Alkyl and Aryl Alkylcarbamates **3a–o**[a] (continued)

| Entry | R | Ar or R′ | Ratio (**2**:**1**) | Time (h) | Product | Yield (%)[b] | GC purity (%) | MS *m/z* [M⁺] | Mp (°C) or bp (°C / mmHg) Crude | Recrystallized (solvent) | Lit. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 29 | Bn | 4-$ClC_6H_4$ | 3:1 | 12 | **3o** | 99 | 99.3 | 261 | 141.3–142.6 | 143.6–144.5 (MeOH) | 141–143[15] |
| 30 | | | 2:1 | 13 | **3o** | 99 | 99.3 | 261 | 141.3–142.6 | | |
| 31 | | | 1:1 | 20 | **3o** | 96 | 100 | 261 | 141.6–142.9 | | |

[a] Unless otherwise noted, the reactions were performed in anhydrous toluene, under reflux in the presence of $Et_3N$.
[b] Unless otherwise noted, yields refer to the crude isolated products.
[c] After 24 h, the reaction practically stopped despite the presence of varying amounts of the starting *S*-methyl *N*-methylthiocarbamate (10% in entry 3, 6% in entry 8 and 2% in entry 11).
[d] Purified by column chromatography (petroleum ether–$Et_2O$, 3:2).
[e] After washing the crude carbamate with anhydrous pentane.
[f] Purified by column chromatography ($CHCl_3$–MeOH, 9.5:0.5).
[g] Excess BnOH could also be removed by distillation of the BnOH/$H_2O$ azeotrope under reduced pressure. Yield of **3d** was 80–85%.
[h] MeOH was used as both reagent and solvent: *S*-methyl *N*-butylthiocarbamate (10 mmol), MeOH (10 mL), $Et_3N$ (20 mmol) were used.
[i] BuOH was used as both reagent and solvent: *S*-methyl *N*-butylthiocarbamate (10 mmol), BuOH (5 mL, entry 14 or 10 mL, entry 20), $Et_3N$ (20 mmol) were used.
[j] Carbamate **3h** is known,[11] but physical data are not reported.
[k] Carbamate **3j** is known,[12] but physical data are not reported.
[l] Carbamate **3k** is mentioned in the literature,[13] but physical and spectral data are not reported.
[m] Excess octyl alcohol was removed by distillation of the alcohol/water azeotrope under reduced pressure.
[n] Purified by column chromatography ($CH_2Cl_2$–EtOAc, 9:1).
[o] By $^1H$ NMR analysis.

As seen in Table 1, the reactions of *S*-methyl *N*-methylthiocarbamate (**1**, R = Me) with equimolar amounts of alcohol or phenol **2** (molar ratio **1**:**2** = 1:1; entries 3, 8 and 11), were very slow and practically stopped after 24 hours despite the presence of varying amounts (2 to 14%) of the starting thiocarbamate in the reaction mixtures. These reactions supplied the corresponding carbamates **3a**, **3c** and **3d** in modest yields (41–64%). The use of an excess of **2** (molar ratio **1**:**2** = 1:2), had a double effect: it greatly shortened the reaction times and supplied purer products in higher yields (compare entries 2, 7 and 10, respectively, with entries 3, 8 and 11). A further increase in the amount of **2** (molar ratio **1**:**2** = 1:3), led to even faster reactions, without affecting the yields or purity of the carbamates **3a–d** (compare entries 1, 4, 6 and 9, respectively, with entries 2, 5, 7 and 10). The alcohol or phenol excess was then recovered almost quantitatively at the end of the reaction. With regard to *S*-methyl *N*-benzylthiocarbamate (**1**, R = Bn), it can be seen that the reactions carried out with equimolar amounts of alcohol or phenol **2** (molar ratio **1**:**2** = 1:1), were still slow (15–24 h), but the corresponding carbamates **3l–o** were supplied in very high yields and high purity (entries 23, 25, 28 and 31). An excess of **2** (molar ratio **1**:**2** = 1:2), drastically shortened the reaction times and had practically no influence on the yields or purity of the products **3** (compare entries 22, 24, 27 and 30 with entries 23, 25, 28 and 31, respectively). A further increase in the amount of **2** (molar ratio **1**:**2** = 1:3), further shortened, though only slightly, the reaction times (compare entries 26 and 29 with entries 27 and 30, respectively). Thus, for the benzylthiocarbamate, the optimal molar ratios of **1**:**2** were found to be 1:2. Furthermore, in these cases, the excess alcohol or phenol were recovered almost quantitatively at the end of the reactions. These reagent molar ratios were also used to obtain the carbamates **3f–k** (entries 13, 15, 17–19 and 21).

The course of the reactions was followed by GC and $^1H$ NMR analyses until the disappearance of the starting thiocarbamates was observed. Under the best conditions, most of the reactions reached completion in times ranging from 4 to 13 hours in the case of the phenols, and from 7 to 12 hours for the alcohols, the sole exceptions being the reactions involving alcohols with a boiling point lower than 115 °C (entries 13 and 19), which required longer times to reach completion (24 h). These last reactions were suitably carried out using the alcohols themselves as both reagent and solvent, at reflux temperature and always in the presence of triethylamine (entries 12, 14 and 20). At the end of the reaction, all the mixtures were diluted with sufficient dichloromethane to form homogeneous solutions with the reaction solvent toluene. When the reagents **2** were phenols, the organic solutions were washed successively with aqueous 5% hydrochloric acid, water, aqueous 5% sodium hydroxide and then again with water. After drying ($Na_2SO_4$) and evaporation of the solvent under reduced pressure, the aryl alkylcarbamates **3a–c**, **3h**, **3i**, **3n** and **3o** were obtained in yields of 80 to 99% (average yield of 7 samples 92%) and with GC purities higher than 99.2%. The basic washing allowed nearly quantitative recovery of the excess phenols. When the reagents **2** were alcohols, the organic solutions were washed with aqueous 5% hydrochloric acid and water. Then the solvent and a part of the excess alcohol were removed under reduced pressure. Further water addition simplified the removal of

any alcohol still present by distillation of the alcohol/water azeotropes under reduced pressure. The crude carbamates were then dried by treatment with chloroform followed by distillation of the chloroform/water azeotropes under reduced pressure. In entries 9–11 and 22, the carbamate/alcohol separation was also achieved by column chromatography, and the excess alcohol was recovered almost quantitatively. Under the best conditions, the yield of the alkyl alkylcarbamates **3d–g** and **3j–m** varied between 88 and 100% (average yield of the 8 considered examples was 95%) and their GC purity was always higher than 99.4%.

When working on a large scale,[10] the triethylamine contained in the reflux liquid could be efficiently recycled in the reaction mixture. Consequently, the reactions could be carried out in the presence of smaller amounts of triethylamine (molar ratio **1**:**2**:$Et_3N$ = 1:2:0.25). Furthermore, when the reagents **2** were alcohols, at the end of the reaction the excess alcohol could be simply recovered by fractional distillation of the mixtures. Another merit of the procedure, when applied on a large scale,[10] was that besides the target products, i.e. the carbamates **3**, almost quantitative recovery of a co-product of industrial interest, methanethiol, as sodium methanethiolate was achieved, with evident economic advantages.

In conclusion, this work offers a general, simple and efficient procedure for the synthesis of alkyl and aryl alkylcarbamates **3** starting from the corresponding *S*-methyl *N*-alkylthiocarbamates **1**. The latter can be prepared by methylthiocarbonylation of primary aliphatic amines with *S*,*S*-dimethyl dithiocarbonate (DMDTC),[5] an easily available[16] liquid reagent that is neither toxic nor hazardous. Therefore this procedure can be considered a valid and safe alternative to traditional methods that use harmful reagents like phosgene, isocyanates and carbon monoxide.

Finally, on comparing the new one-step procedure for the preparation of alkyl and aryl alkylcarbamates **3** starting from *S*-methyl *N*-alkylthiocarbamates **1**, with the other, recently reported,[4] three-step procedure, carried out in a one-pot fashion via carbamoyl chlorides and isocyanates, some useful observations can be made. Although both procedures supply the target products in high yields and high purity, the new one-step procedure is simpler and avoids the use of chlorine. However, it requires relatively longer reaction times and therefore appears more suitable for laboratory preparations or, on a large scale, for batch processes. Instead, the three-step procedure, certainly more laborious for laboratory preparations, appears more suitable for continuous processes in large-scale applications.

Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker Avance 200 spectrometer at 200 MHz and 50 MHz, respectively, in $CDCl_3$. MS spectra were recorded on an AT 5973N mass-selective detector connected to an AT 6890N GC, cross-linked methyl silicone capillary column. Details for the reactions and yields for the pure (GC, GC-MS, $^1H$ NMR) alkyl and aryl alkylcarbamates **3a–o** 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, $^1H$ NMR) with those reported in the literature. All the amines were purchased from Aldrich and used without further purification. *S*,*S*-Dimethyl dithiocarbonate (DMDTC) was supplied from Oxon Italia S.p.A. (Italy)[17] or prepared as described in the literature.[16]

### *S*-Methyl *N*-Alkylthiocarbamates 1

Prepared by methylthiocarbonylation of aliphatic primary amines (20 mmol) with *S*,*S*-dimethyl dithiocarbonate (10 mmol) in $H_2O$ at 20–25 °C, according to the procedure previously reported.[5] The crude *S*-methyl *N*-alkylthiocarbamates **1** were obtained in excellent yields and with a high degree of purity, and the excess amine was recovered in quantitative yield. Reaction times, yields and GC purity of the crude products were as follows: *S*-methyl *N*-methylthiocarbamate (**1**, R = Me; 15 min, ~100%, 99.8%), *S*-methyl *N*-butylthiocarbamate (**1**, R = Bu; 2 h, ~100%, 100%), *S*-methyl *N*-cyclohexylthiocarbamate (**1**, R = *c*-Hex; 24 h, 95%, 99%), and *S*-methyl *N*-benzylthiocarbamate (**1**, R = Bn; 15 h, 98%, 99.7%). All the thiocarbamates **1** were directly used in the next step, without further purification.

### Direct Conversion of *S*-Methyl *N*-Alkylthiocarbamates 1 into Alkyl and Aryl Alkylcarbamates 3a–o; Typical Procedures

#### 4-Bromophenyl Benzylcarbamate (3n)

Table 1, Entry 27: A mixture of the crude *S*-methyl *N*-benzylthiocarbamate (**1**; R = Bn; 1.81 g, 10 mmol), 4-bromophenol (**2**; Ar = 4-$BrC_6H_4$; 3.46 g, 20 mmol), and $Et_3N$ (2.22 g, 22 mmol) in anhydrous toluene (10–15 mL) was heated to reflux with an oil bath maintained at 120–123 °C, under stirring. A solution was obtained. Progress of the reaction was monitored by GC and $^1H$ NMR analyses that showed a progressive decrease in the amount of the starting thiocarbamate **1** and a progressive increase in the amount of 4-bromophenyl benzylcarbamate (**3n**). The reaction was complete after 7 h (disappearance of the thiocarbamate). The reaction mixture was diluted with sufficient $CH_2Cl_2$ to form a homogeneous solution with the reaction solvent toluene (150 mL). This solution was washed successively with aq 5% HCl (60 mL), $H_2O$ (60 mL), aq 5% NaOH (60 mL), and then with $H_2O$ (60 mL), dried ($Na_2SO_4$) and evaporated under reduced pressure to give the title compound **3n**. $^1H$ NMR and MS data were identical to those reported.[4]

Yield: 2.94 g (96%, based on thiocarbamate); 100% GC purity; mp 168.2–169.4 °C, 168.3–169.4 ($CHCl_3$) (Lit.[4] 167.9–168.8 °C).

The basic solution was acidified with aq 5% HCl, extracted with $CH_2Cl_2$ (2 × 80 mL), dried ($Na_2SO_4$) and evaporated under reduced pressure to give pure 4-bromophenol (GC, GC-MS, $^1H$ NMR) in quantitative yield (1.73 g).

Carbamates **3a–c**, **3h**, **3i**, **3n** and **3o** (entries 1–8, 17, 18, 26–31) were prepared according to the above procedure and the starting phenols were almost quantitatively recovered.

#### Benzyl Methylcarbamate (3d)

Table 1, Entry 9: A mixture of the crude *S*-methyl *N*-methylthiocarbamate (**1**; R = Me; 1.05 g, 10 mmol), benzyl alcohol (**2**; R′ = Bn; 3.24 g, 30 mmol), and $Et_3N$ (3.33 g, 33 mmol) in anhydrous toluene (10–15 mL) was heated to reflux with an oil bath maintained at 120–123 °C, under stirring. A solution was obtained. Progress of the reaction was monitored by GC and $^1H$ NMR analyses that showed a progressive decrease in the amount of the starting thiocarbamate **1** and a progressive increase in the amount of benzyl methylcarbamate (**3d**). The reaction was complete after 7 h (disappearance of the thiocarbamate). The reaction mixture was diluted with sufficient

$CH_2Cl_2$ to form a homogeneous solution with the reaction solvent toluene (150 mL). This solution was washed successively with aq 5% HCl (60 mL) and $H_2O$ (60 mL), dried ($Na_2SO_4$) and evaporated under reduced pressure. The crude oily residue, which consisted of **3d** and benzyl alcohol, was purified by column chromatography ($CHCl_3$–MeOH, 9.5:0.5). The first eluted product was benzyl methylcarbamate [**3d**; 1.45 g (88% yield); 100% GC purity; colorless oil; bp 124–125 °C/0.6 mm Hg (Lit.[4] 118 °C/0.5 mm Hg)]. The second eluted product was the pure benzyl alcohol [2.05 g (95%)].

Alternatively, the crude oily residue was worked up as follows: $H_2O$ (150 mL) was added and the $H_2O$/benzyl alcohol azeotrope was distilled under reduced pressure. The oil was dried by subsequent addition of $CHCl_3$ (3 × 20 mL) and distillation under reduced pressure of the $CHCl_3/H_2O$ azeotropes to give **3d** [1.32–1.40 g (80–85%); 100% GC purity].

When working on a large scale,[10] excess benzyl alcohol and $Et_3N$ could be recovered almost quantitatively by direct fractional distillation of the reaction mixture.

Carbamates **3f** (entry 13) and **3g** and **3j**–**m** (entries 15, 16, 19 and 21–25) were prepared according to the above procedure. In particular, excess butyl (entries 13 and 19) and propargyl (entry 15) alcohols were removed by direct distillation of the reaction mixtures under reduced pressure. Excess octyl (entry 21) and benzyl (entries 24 and 25) alcohols were removed by distillation of the water/alcohol azeotropes under reduced pressure. Excess hexadecyl alcohol (entry 22) was removed by column chromatography ($CH_2Cl_2$–EtOAc, 9:1) and recovered pure in 95% yield.

**Butyl Butylcarbamate (3f)**

Table 1, Entry 14: A mixture of the crude *S*-methyl *N*-butylthiocarbamate (**1**; R = Bu; 1.47 g, 10 mmol), 1-butanol (**2**; R′ = Bu; 5 mL), and $Et_3N$ (2.22 g, 22 mmol) was heated at reflux with an oil bath maintained at 120–123 °C, under stirring. After 4 h, GC and GC-MS analyses of the solution showed the disappearance of the starting thiocarbamate and the presence of butyl butylcarbamate (**3f**) as the only product. Excess butanol and $Et_3N$ were removed by distillation under reduced pressure to give the title compound **3f** [1.70 g (98%); 99.9% GC purity].

When working on a large scale,[10] excess butanol and $Et_3N$ could be recovered almost quantitatively by direct fractional distillation of the reaction mixture.

Methyl butylcarbamate (**3e**) was prepared according to the above procedure (entry 12).

Yields, GC purity and physical data (mp and bp) of all the carbamates **3a**–**o** are reported in Table 1. Spectral data ($^1$H NMR and MS) of carbamates **3b**–**d**, **3g**, **3i** and **3n** were identical to those previously prepared.[4]

**4-Bromophenyl Methylcarbamate (3a)**

Only $^{13}$C NMR data are reported in the literature.[18]

$^1$H NMR: δ = 2.89 (d, *J* = 4.6 Hz, 3 H, $CH_3$), 5.11 (m, 1 H, NH), 6.96 (d, *J* = 8.8 Hz, 2 H, ArH), 7.46 (d, *J* = 8.8 Hz, 2 H, ArH).

MS (EI, 70 eV): *m*/*z* (%) = 229 (1) [M$^+$], 174 (96), 172 (100), 93 (20), 65 (36), 63 (13), 57 (24), 56 (9).

**Methyl Butylcarbamate (3e)**

$^1$H NMR: δ = 0.87 (t, *J* = 6.5 Hz, 3 H, C*H*$_3$CH$_2$), 1.20–1.33 (m, 2 H, CH$_3$C*H*$_2$), 1.33–1.50 (m, 2 H, CH$_3$CH$_2$C*H*$_2$), 3.11 (d, *J* = 6.0 Hz, 2 H, C*H*$_2$NH), 3.61 (s, 3 H, $OCH_3$), 4.89 (m, 1 H, NH). Similar to that reported.[19]

MS (EI, 70 eV): *m*/*z* (%) = 131 (10) [M$^+$], 89 (7), 88 (100), 76 (6), 59 (10), 57 (6), 44 (21).

**Butyl Butylcarbamate (3f)**

$^1$H NMR: δ = 0.91 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 0.92 (t, *J* = 7.2 Hz, 3 H, $CH_3$), 0.95–1.65 (2 × m overlapping, 8 H, 2 × C*H*$_2$C*H*$_2$CH$_3$), 3.16 (app q, *J* = 6.4 Hz, 2 H, C*H*$_2$NH), 4.04 (t, *J* = 6.5 Hz, 2 H, $CH_2O$), 4.67 (m, 1 H, NH). Identical to that reported.[20]

MS (EI, 70 eV): *m*/*z* (%) = 173(9) [M$^+$], 131 (10), 130 (100), 118 (85), 116 (12), 100 (14), 88 (59), 75 (8), 74 (16), 62 (12), 57 (89), 56 (39), 55 (13).

**Butyl 4-Methoxyphenylcarbamate (3h)**

$^1$H NMR: δ = 0.95 (t, *J* = 7.0 Hz, 3 H, $CH_3$), 1.29–1.44 (m, 2 H, CH$_3$C*H*$_2$), 1.47–1.76 (m, 2 H, CH$_3$CH$_2$C*H*$_2$), 3.25 (app q, *J* = 6.5 Hz, 2 H, C*H*$_2$NH), 3.79 (s, 3 H, $OCH_3$), 5.11 (m, 1 H, NH), 6.87 (d, *J* = 8.8 Hz, 2 H, ArH), 7.05 (d, *J* = 8.8 Hz, 2 H, ArH). Similar to that reported.[11]

MS (EI, 70 eV): *m*/*z* (%) = 223 (1) [M$^+$], 125 (9), 124 (100), 109 (60), 81 (19), 56 (9).

**Butyl Benzylcarbamate (3j)**

$^1$H NMR: δ = 0.94 (t, *J* = 7.3 Hz, 3 H, $CH_3$), 1.25–1.47 (m, 2 H, CH$_3$C*H*$_2$), 1.54–2.38 (m, 2 H, CH$_3$CH$_2$C*H*$_2$), 4.10 (t, *J* = 6.6 Hz, 2 H, $OCH_2$), 4.37 (d, *J* = 5.9 Hz, 2 H, C*H*$_2$NH), 5.07 (m, 1 H, NH), 7.24–7.40 (m, 5 H, ArH). Similar to that reported.[12]

MS (EI, 70 eV): *m*/*z* (%) = 207 (11) [M$^+$], 151 (14), 150 (100), 133 (30), 132 (13), 106 (37), 105 (19), 104 (20), 91 (60), 79 (16), 78 (10), 77 (17), 65 (10), 56 (10), 51 (10).

**Octyl Benzylcarbamate (3k)**

The title compound is mentioned in the literature,[13] but physical and spectral data were not reported.

$^1$H NMR: δ = 0.89 (t, *J* = 5.7 Hz, 3 H, $CH_3$), 1.15–1.45 [m, 10 H, CH$_3$(C*H*$_2$)$_5$CH$_2$], 1.59 (m, 2 H, C*H*$_2$CH$_2$O), 4.09 (t, *J* = 6.4 Hz, 2 H, CH$_2$C*H*$_2$O), 4.37 (d, *J* = 5.5 Hz, C*H*$_2$NH), 5.03 (m, NH), 7.31 (m, 5 H, ArH).

$^{13}$C NMR: δ = 15.53 ($CH_3$), 24.08, 27.30, 30.48, 30.65, 33.22 ($CH_2$), 46.47 (*C*H$_2$NH), 66.68 ($CH_2O$), 128.87, 130.07 (CH), 140.08 (C), 158.25 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 263 (8) [M$^+$], 151 (23), 150 (100), 134 (16), 132 (7), 106 (25), 105 (13), 104 (10), 91 (35), 79 (8), 77 (8), 69 (7), 56 (8), 55 (10).

Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32. Found: C, 73.05; H, 9.63; N, 5.38.

**Hexadecyl Benzylcarbamate (3l)**

$^1$H NMR: δ = 3.07 (t, *J* = 6.3 Hz, 3 H, $CH_3$), 1.17–1.37 [m, 28 H, CH$_3$(C*H*$_2$)$_{14}$CH$_2$], 1.55–1.68 (m, 2 H, C*H*$_2$CH$_2$O), 4.10 (t, *J* = 6.4 Hz, 2 H, CH$_2$C*H*$_2$O), 4.38 (d, *J* = 5.6 Hz, C*H*$_2$NH), 4.95 (m, NH), 7.27–7.38 (m, 5 H, ArH).

MS (EI, 70 eV): *m*/*z* (%) = 375 (1) [M$^+$], 150 (55), 133 (76), 132 (29), 105 (32), 104 (38), 97 (23), 91 (65), 83 (29), 77 (28), 69 (26), 57 (26), 55 (31).

$^{13}$C NMR: δ = 15.54 ($CH_3$), 24.12, 27.30, 30.47, 30.73, 30.79, 31.01, 31.11, 33.45 ($CH_2$), 66.69 ($CH_2O$), 46.50 (*C*H$_2$NH), 128.87, 130.07 (CH), 140.06 (C), 158.21 (C=O).

Anal. Calcd for $C_{24}H_{41}NO_2$: C, 76.75; H, 11.00; N, 3.73. Found: C, 76.84; H, 11.05; N, 3.78.

**Benzyl Benzylcarbamate (3m)**

$^1$H NMR: δ = 4.40 (d, *J* = 5.8 Hz, 2 H, C*H*$_2$NH), 5.16 (s, 2 H, $OCH_2$), 5.24 (m, 1 H, NH), 7.10–7.50 (m, 10 H, ArH). Similar to that reported.[21]

MS (EI, 70 eV): *m*/*z* (%) = 241 (1) [M$^+$], 150 (90), 133 (27), 132 (11), 108 (42), 107 (21), 106 (25), 105 (14), 104 (15), 92 (12), 91 (100), 79 (38), 78 (12), 77 (30), 65 (18), 51 (13).

**4-Chlorophenyl Benzylcarbamate (3o)**

The title compound is known,[15] but spectral data were not reported.

$^1$H NMR: δ = 4.45 (d, *J* = 6.0 Hz, 2 H, $CH_2$), 7.10 (d, *J* = 8.8 Hz, 2 H, ArH), 7.32 (d, *J* = 8.8 Hz, 2 H, ArH), 7.34–7.42 (m, 5 H, ArH).

$^{13}$C NMR: δ = 46.78 ($CH_2$), 124.36, 129.15, 129.23, 130.25, 130.75 (CH), 132.07, 139.26, 150.98 (C), 155.72 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 261 (1) [M$^+$], 133 (57), 132 (23), 130 (32), 129 (8), 128 (100), 105 (23), 104 (28), 91 (60), 78 (14), 77 (21), 65 (28), 64 (9), 63 (12), 51 (15), 50 (10).

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