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Synthesis of *N*-Aryl *S*-Alkylthiocarbamates

Mamoru Koketsu, Chikashi Kobayashi, and Hideharu Ishihara

Department of Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan

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ABSTRACT: *Several N-aryl S-alkylthiocarbamates were synthesized by reactions of isocyanates with LiAlHSH and then with alkyl halides.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:374–378, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10163

INTRODUCTION

Thiocarbamates have been used as key intermediates for the synthesis of ureas [1] and isocyanates [2] and are very important moieties in pesticides [3]. However, only a limited number of methods have been reported for the preparation of the thiocarbamates. For example, *S*-allylic thiocarbamates were obtained from *O*-allylic thiocarbamates by 1,3-allyl migration from the oxygen to the sulfur atom [4]. Other routes are the reactions of alkyl thiocyanates with alcohols [5], and of amines with elemental sulfur and carbon monoxide in the presence of selenium [6]. A facile method for the preparation of thiocarbamates would certainly be very useful. Recently, we developed a novel selenating reagent [7], LiAlHSeH which is generated by the stirring selenium powder with $LiAlH_4$ in THF. This reagent is useful for preparing a variety of selenium containing compounds [8]. However, application of same procedure to the sulfur atom, while reasonable, has not yet been been demonstrated. In the present study, we investigated the preparation of various thiocarbamates from the corresponding isocyanates **1** and alkyl halides **3**, using LiAlHSH **2**. Herein, we report a new method for preparation of *S*-alkyl thiocarbamates **4** and confirm the usefulness of LiAlHSH as a reagent for the introduction of sulfur atom.

RESULTS AND DISCUSSION

The reaction leading to *N*-aryl *S*-alkylthiocarbamates **4** is shown in Scheme 1. Phenyl isocyanate **1a** was added to an anhydrous THF solution of LiAlHSH **2** [9]. The reaction mixture was stirred at room temperature for 1 h under an argon atmosphere. A solution of methyl iodide **3a** in THF was added to the reaction mixture at room temperature. The resulting reaction mixture was stirred for an additional 3 h.

After workup, *S*-methyl *N*-phenylthiocarbamate **4a** was obtained in 84% yield. Reactions of three isocyanates **1** with nine alkyl halides **3** also gave the corresponding *N*-aryl *S*-alkylthiocarbamates **4** (Table 1). The yield using alkyl halides bearing longer carbon chains tended to decrease because of their reduced electrophilicity. These results confirm that LiAlHSH **2** affords a variety of *N*-aryl *S*-alkylthiocarbamates, showing a reactivity similar to LiAlHSeH [8b]. The ^{13}C NMR spectra of **4** in $CDCl_3$ show interesting spectral features at 20°C. There is significant line broadening of the peaks of C1, C2, C4, C6, and C7, while those of C3, C5, and alkyl carbons gave typically sharp peaks (Fig. 1, upper). These spectral features were highly dependent on the conditions of the NMR measurement. For example, the broad signals of **4** became sharper when the spectrum was measured in DMSO-d_6 or in $CDCl_3$ at lower temperatures (0 and −20°C). The ^{13}C NMR spectra measured in $CDCl_3$ at −40°C showed sharp peaks similar to ordinary spectra along with new small satellite peaks (Fig. 1, lower). These interesting observations in the NMR

Correspondence to: Mamoru Koketsu; e-mail: koketsu@cc.gifu-u.ac.jp.
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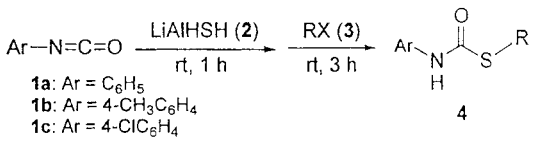


SCHEME 1

spectra are predicted based on equilibrium in **4**, between the major *s-trans* and the minor *s-cis* forms (Scheme 2), as was previously observed in the NMR spectra of *Se*-aryl *N*-alkylselenocarbamates [8b].

In conclusion, various *S*-aryl *N*-alkylthiocarbamates have been synthesized by reacting isocyanates **1** with LiAlHSH **2** and then with alkyl halides. It was confirmed that LiAlHSH **2** behaves similar to LiAlHSeH [7], and represents an excellent reagent for the introduction of sulfur.

EXPERIMENTAL

Melting points were determined by use of Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were measured on Perkin-Elmer 1600 spectrometer. ^{1}H and ^{13}C spectra were recorded on a JEOL-JNM-α400 (400 MHz) spectrometer. Mass spectra were obtained on a Shimadzu 9020-DF mass spectrometer. Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use.

S-Methyl N-phenylthiocarbamate **4a**. Phenyl isocyanate **1a** (0.22 ml, 2.0 mmol) was added to a THF solution (10 ml) of LiAlHSH **2** (1.0 mmol). The reaction mixture was stirred at room temperature for 1 h. Methyl iodide **3a** (0.06 ml, 1.0 mmol) was added to the reaction mixture. The resulting reaction mixture was stirred at room temperature for 3 h. The mixture was extracted with dichloromethane and washed with water. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with dichloromethane/hexane (1:2) to give **4a** 0.14 g (84%) as white crystals; mp 71.2–72.8°C; IR (KBr) 1661, 3288 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 2.42 (3H, s, CH_3), 7.11 (1H, t, $J = 7.2$ Hz, Ar), 7.12 (1H, br s, NH), 7.31 (2H, t, $J = 7.2$ Hz, Ar), 7.41 (2H, d, $J = 7.2$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 12.6, 119.8, 124.4, 129.1, 137.7, (Ar), 162.6; MS (CI): $m/z = 168$ [$M^+ + 1$].

S-Ethyl N-phenylthiocarbamate **4b**. White crystals; mp 63.9–65.1°C; IR (KBr) 1651, 3281 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 1.33 (3H, t, $J = 7.2$ Hz, CH_3), 2.98 (2H, q, $J = 7.2$ Hz, CH_2), 7.09 (1H, t, $J = 7.2$ Hz, Ar), 7.21 (1H, br s, NH), 7.30 (2H, t, $J = 7.2$ Hz, Ar), 7.41 (2H, d, $J = 7.2$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 15.5, 24.7, 119.7, 124.4, 129.1, 137.6 (Ar), 165.8; MS (CI): $m/z = 182$ [$M^+ + 1$].

S-Propyl N-phenylthiocarbamate **4c**. White crystals; mp 73.2–75.6°C; IR (KBr) 1653, 3280 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 1.00 (3H, t, $J = 7.6$ Hz, CH_3), 1.67 (2H, m, CH_2), 2.95 (2H, t, $J = 7.6$ Hz, CH_2), 7.02 (1H, br s, NH), 7.10 (1H, t, $J = 7.6$ Hz, Ar), 7.31 (2H, t, $J = 7.6$ Hz, Ar), 7.41 (2H, d, $J = 7.6$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 13.2, 23.6, 32.2, 119.7–137.7 (Ar), 165.9; MS (CI): $m/z = 196$ [$M^+ + 1$].

S-Butyl N-phenylthiocarbamate **4d**. White crystals; mp 64.3–65.0°C; IR (KBr) 1652, 3287 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 0.92 (3H, t, $J = 7.6$ Hz, CH_3), 1.42 (2H, m, $J = 7.6$ Hz, CH_2), 1.64 (2H, quint, $J = 7.6$ Hz, CH_2), 2.97 (2H, t, $J = 7.6$ Hz, CH_2), 7.09 (1H, t, $J = 7.2$ Hz, Ar), 7.13 (1H, br s, NH), 7.30 (2H, t, $J = 7.2$ Hz, Ar), 7.40 (2H, d, $J = 7.2$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 13.6, 21.8, 29.9, 32.3, 119.6–137.8 (Ar), 166.0; MS (CI): $m/z = 210$ [$M^+ + 1$].

TABLE 1 Synthesis of *N*-Aryl *S*-Alkylthiocarbamate

	*Thiocarbamate (**4**), Yield (%)*[a]		
*RX (**3**)*	*Ar = C_6H_5 (**4a–4i**)*	*Ar = 4-$CH_3C_6H_4$ (**4j–4r**)*	*Ar = 4-ClC_6H_4 (**4s–4v**)*
CH_3I	84	59	–[b]
C_2H_5I	71	51	47
$CH_3(CH_2)_2I$	66	50	–[b]
$CH_3(CH_2)_3I$	54	46	–[b]
$(CH_3)_2CH(CH_2)_2I$	50	52	–[b]
$CH_3(CH_2)_7Br$	25	24	–[b]
$C_6H_5CH_2Br$	55	36	35
$C_6H_5(CH_2)_2Br$	44	32	24
$C_6H_5(CH_2)_3Br$	36	44	23

[a]Isolated yield.
[b]Not tried.

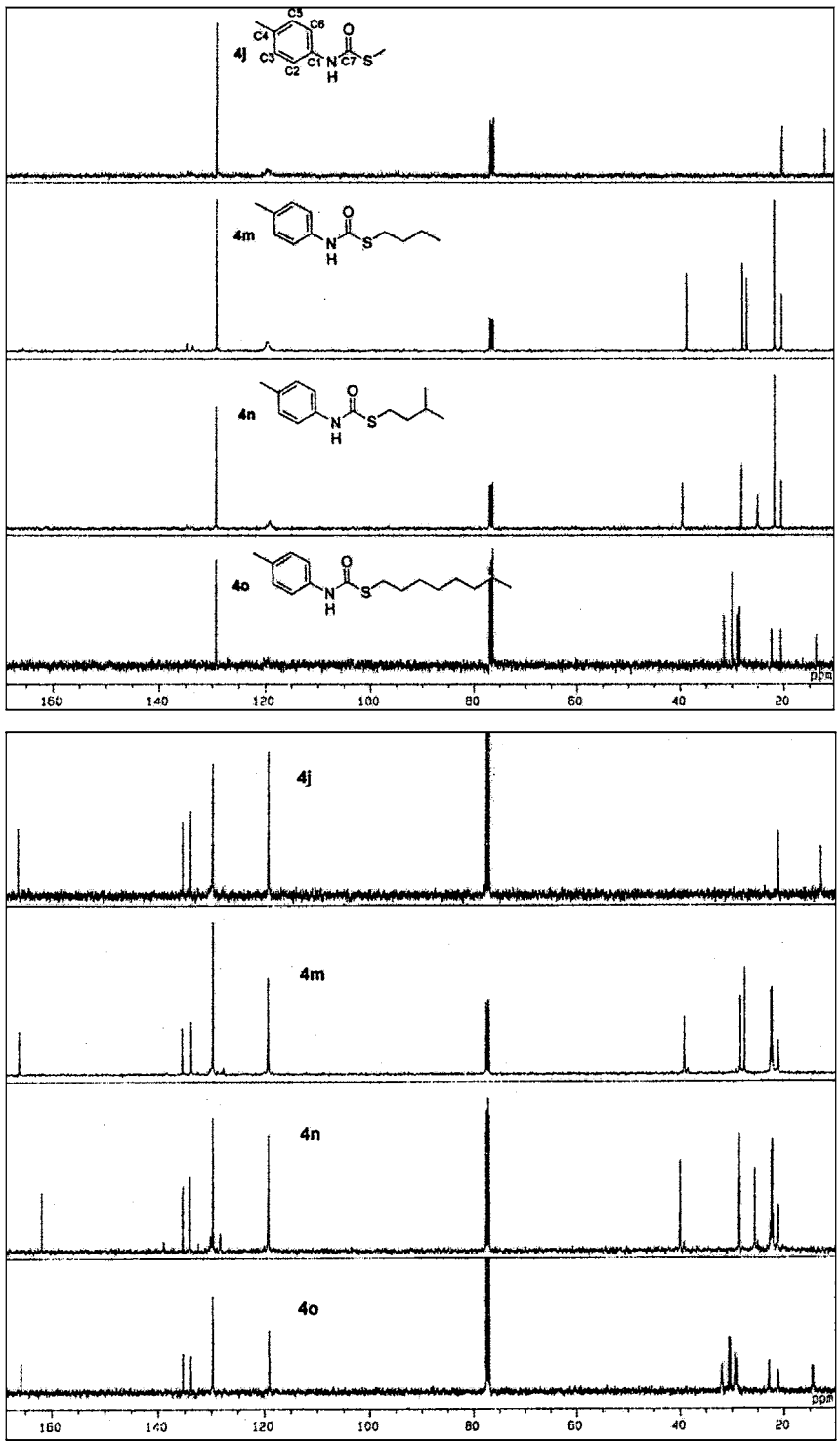
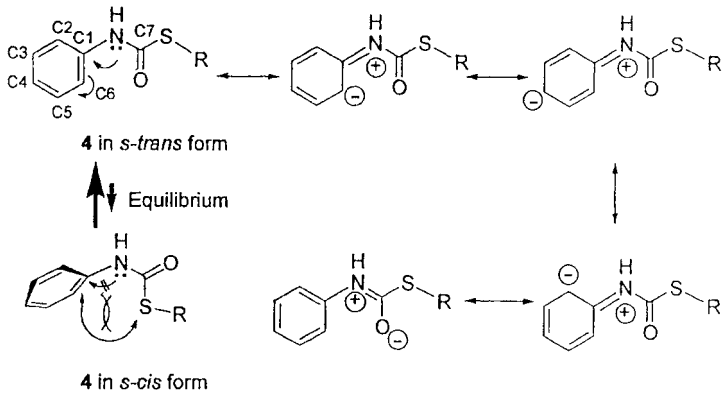


FIGURE 1 ^{13}C NMR spectra of compounds **4** at 20°C (upper) and −40°C (lower).

S-Isopentyl N-phenylthiocarbamate **4e**. White crystals; mp 66.1–69.3°C; IR (KBr) 1655, 3290 cm^{-1}; ^1H NMR ($CDCl_3$); δ 0.92 (6H, t, $J = 6.8$ Hz, CH_3), 1.54 (2H, q, CH_2), 1.68 (1H, m, CH), 2.97 (2H, t, $J = 8.0$ Hz, CH_2), 7.09 (1H, t, $J = 7.2$ Hz, Ar), 7.19 (1H, br s, NH), 7.30 (2H, t, $J = 7.2$ Hz, Ar), 7.41 (2H, d, $J = 7.2$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 22.1, 27.4, 28.3, 30.8, 39.1, 119.6–137.7 (Ar), 165.9; MS (CI): $m/z = 224$ $[M^+ + 1]$.

S-Octyl N-phenylthiocarbamate **4f**. White crystals; mp 56.1–58.9°C; IR (KBr) 1658, 3328 cm^{-1}; ^1H



SCHEME 2

NMR ($CDCl_3$); δ 0.86 (3H, t, $J = 6.8$ Hz, CH_3), 1.33 (10H, d, $J = 6.8$, CH_2), 1.65 (2H, m, CH_2), 2.96 (2H, t, $J = 6.8$ Hz, CH_2), 7.09 (1H, t, $J = 7.2$ Hz, Ar), 7.10 (1H, br s, NH), 7.30 (2H, t, $J = 7.2$ Hz, Ar), 7.41 (2H, d, $J = 7.2$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 14.0, 22.6, 28.7, 29.0, 29.1, 30.2, 30.3, 31.7, 119.6–137.7 (Ar), 165.9; MS (CI): $m/z = 266$ [$M^+ + 1$].

S-Benzyl N-phenylthiocarbamate **4g**. White powder; mp 92.1–94.2°C; IR (KBr) 1653, 3250 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 4.22 (2H, s, CH_2), 7.08–7.40 (10H, m, Ar), 7.10 (1H, br s, NH); ^{13}C NMR ($CDCl_3$); δ 34.4, 119.8–137.8 (Ar), 165.1; MS (CI): $m/z = 244$ [$M^+ + 1$].

S-Phenetyl N-phenylthiocarbamate **4h**. White crystals; mp 108.1–110.3°C; IR (KBr) 1652, 3382 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 2.96 (2H, t, $J = 6.8$ Hz, CH_2), 3.21 (2H, t, $J = 7.7$ Hz, CH_2), 7.08–7.40 (10H, m, Ar), 7.43 (1H, br s, NH); ^{13}C NMR ($CDCl_3$); δ 31.5, 36.6, 119.7–139.9 (Ar), 165.5; MS (CI): $m/z = 258$ [$M^+ + 1$].

S-3-Phenyl-propyl N-phenylthiocarbamate **4i**. White crystals; mp 78.3–79.8°C; IR (KBr) 1652, 3386 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 1.99 (2H, quint, $J = 7.2$ Hz, CH_2), 2.73 (2H, t, $J = 7.2$ Hz, CH_2), 2.99 (2H, t, $J = 7.2$ Hz, CH_2), 7.08–7.41 (10H, m, Ar), 7.17 (1H, br s, NH); ^{13}C NMR ($CDCl_3$); δ 29.7, 31.8, 34.7, 119.6–141.5 (Ar), 165.7; MS (CI): $m/z = 272$ [$M^+ + 1$].

S-Methyl N-(4-methylphenyl)thiocarbamate **4j**. Yellow crystals; mp 102.1–103.5°C; IR (KBr) 1654, 3242 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 2.30 (3H, s, CH_3), 2.39 (3H, s, CH_3), 7.10 (1H, d, $J = 8.4$ Hz, Ar), 7.27 (1H, br s, NH), 7.28 (2H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 12.5, 20.7, 119.9–135.0, (Ar), 166.3; MS (CI): $m/z = 182$ [$M^+ + 1$].

S-Ethyl N-(4-methylphenyl)thiocarbamate **4k**. White crystals; mp 81.0–81.5°C; IR (KBr) 1654, 3260 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 1.33 (3H, t, $J = 7.2$ Hz, CH_3), 2.30 (3H, s, CH_3), 2.96 (2H, q, $J = 7.2$ Hz, CH_2), 7.10 (1H, d, $J = 8.4$ Hz, Ar) , 7.21 (1H, br s, NH), 7.28 (2H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 15.5, 20.8, 119.8–134.6 (Ar), 165.8; MS (CI): $m/z = 196$ [$M^+ + 1$].

S-Propyl N(4-methylphenyl)thiocarbamate **4l**. White crystals; mp 74.2–75.8°C; IR (KBr) 1653, 3294 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 1.00 (3H, t, $J = 7.6$ Hz, CH_3), 1.68 (2H, m, CH_2), 2.30 (3H, s, CH_3), 2.95 (2H, t, $J = 7.6$ Hz, CH_2), 7.03 (1H, br s, NH), 7.10 (1H, d, $J = 8.4$ Hz, Ar) , 7.28 (2H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 13.2, 20.8, 23.6, 32.1, 119.9–135.2 (Ar), 166.0; MS (CI): $m/z = 210$ [$M^+ + 1$].

S-Butyl N-(4-methylphenyl)thiocarbamate **4m**. White crystals; mp 73.9–75.1°C; IR (KBr) 1651, 3297 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 0.91 (3H, t, $J = 7.6$ Hz, CH_3), 1.40 (2H, m, $J = 7.6$ Hz, CH_2), 1.62 (2H, quint, $J = 7.6$ Hz, CH_2), 2.29 (3H, s, CH_3), 2.95 (2H, t, $J = 7.6$ Hz, CH_2), 7.08 (1H, d, $J = 8.4$ Hz, Ar), 7.23 (1H, br s, NH), 7.28 (2H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 13.5, 20.7, 21.8, 29.9, 32.3, 119.9–135.1 (Ar), 166.0; MS (CI): $m/z = 224$ [$M^+ + 1$].

S-Isopentyl N-(4-methylphenyl)thiocarbamate **4n**. White crystals; mp 33.1–35.6°C; IR (KBr) 1657, 3318 cm^{-1}; ^{1}H NMR ($CDCl_3$); δ 0.92 (6H, t, $J = 6.8$ Hz, CH_3), 1.53 (2H, q, CH_2), 1.67 (1H, m, CH), 2.30 (3H, s, CH_3), 2.96 (2H, t, $J = 7.2$ Hz, CH_2), 7.06 (1H, br s, NH), 7.10 (1H, d, $J = 8.4$ Hz, Ar), 7.28 (2H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 20.8, 22.1, 27.4, 28.3, 30.8, 39.1, 120.0–135.1 (Ar), 164.2; MS (CI): $m/z = 238$ [$M^+ + 1$].

S-Octyl N-(4-methylphenyl)thiocarbamate **4o**. Yellow crystals; mp 61.0–62.1°C; IR (KBr) 1650, 3301 cm^{-1}; ^1H NMR ($CDCl_3$); δ 0.87 (3H, t, $J = 6.8$ Hz, CH_3), 1.31 (10H, d, $J = 6.8$, CH_2), 1.64 (2H, quint, $J = 6.8$ Hz, CH_2), 2.30 (3H, s, CH_3), 2.95 (2H, t, $J = 6.8$ Hz, CH_2), 7.02 (1H, br s, NH), 7.10 (1H, d, $J = 8.4$ Hz, Ar), 7.28 (2H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 14.0, 20.8, 22.6, 28.7, 29.0, 29.1, 30.2, 30.3, 31.7, 119.8–135.1 (Ar), 165.9; MS (CI): $m/z = 280$ [$M^+ + 1$].

S-Benzyl N-(4-methylphenyl)thiocarbamate **4p**. White powder; mp 109.1–110.3°C; IR (KBr) 1653, 3250 cm^{-1}; ^1H NMR ($CDCl_3$); δ 2.30 (3H, s, CH_3), 4.21 (2H, s, CH_2), 7.02 (1H, br s, NH), 7.09–7.36 (9H, m, Ar); ^{13}C NMR ($CDCl_3$); δ 20.8, 34.4, 119.9–137.9 (Ar), 166.2; MS (CI): $m/z = 258$ [$M^+ + 1$].

S-Phenetyl N-(4-methylphenyl)thiocarbamate **4q**. White crystals; mp 97.5–98.7°C; IR (KBr) 1651, 3270 cm^{-1}; ^1H NMR ($CDCl_3$); δ 2.29 (3H, s, CH_3), 2.71 (2H, t, $J = 7.8$ Hz, CH_2), 2.97 (2H, t, $J = 7.8$ Hz, CH_2), 7.08–7.29 (9H, m, Ar), 7.13 (1H, br s, NH); ^{13}C NMR ($CDCl_3$); δ 20.8, 29.6, 31.8, 119.9–141.1 (Ar), 167.7; MS (CI): $m/z = 272$ [$M^+ + 1$].

S-3-Phenyl-propyl N-(4-methylphenyl)thiocarbamate **4r**. White crystals; mp 85.3–86.0°C; IR (KBr) 1653, 3274 cm^{-1}; ^1H NMR ($CDCl_3$); δ 1.98 (2H, quint, $J = 7.6$ Hz, CH_2), 2.29 (3H, s, CH_3), 2.71 (2H, t, $J = 7.6$ Hz, CH_2), 2.97 (2H, t, $J = 7.6$ Hz, CH_2), 7.08–7.29 (9H, m, Ar), 7.13 (1H, br s, NH); ^{13}C NMR ($CDCl_3$); δ 20.8, 29.6, 31.8, 34.7, 119.9–141.1 (Ar), 167.7; MS (CI): $m/z = 286$ [$M^+ + 1$].

S-Ethyl N-(4-chlorophenyl)thiocarbamate **4s**. White crystals; mp 95.1–96.2°C; IR (KBr) 1651, 3271 cm^{-1}; ^1H NMR ($CDCl_3$); δ 1.33 (3H, t, $J = 7.6$ Hz, CH_3), 2.98 (2H, q, $J = 7.6$ Hz, CH_2), 7.13 (1H, br s, NH), 7.26 (2H, t, $J = 8.4$ Hz, Ar), 7.36 (2H, t, $J = 8.4$ Hz, Ar); ^{13}C NMR ($CDCl_3$); δ 15.4, 24.7, 120.8–136.2 (Ar), 166.0; MS (CI): $m/z = 216$ [$M^+ + 1$].

S-Benzyl N-(4-chlorophenyl)thiocarbamate **4t**. White powder; mp 115.0–116.3°C; IR (KBr) 1649, 3244 cm^{-1}; ^1H NMR ($CDCl_3$); δ 4.21 (2H, s, CH_2), 7.07 (1H, br s, NH), 7.11–7.35 (9H, m, Ar); ^{13}C NMR ($CDCl_3$); δ 34.4, 121.0–137.6 (Ar), 165.4; MS (CI): $m/z = 278$ [$M^+ + 1$].

S-Phenetyl N-(4-chlorophenyl)thiocarbamate **4u**. White crystals; mp 120.1–121.9°C; IR (KBr) 1651, 3293 cm^{-1}; ^1H NMR ($CDCl_3$); δ 2.96 (2H, t, $J = 7.8$ Hz, CH_2), 3.22 (2H, t, $J = 7.8$ Hz, CH_2), 7.03 (1H, br s, NH), 7.23–7.37 (9H, m, Ar); ^{13}C NMR ($CDCl_3$); δ 31.6, 36.5, 120.8–139.8 (Ar), 165.6; MS (CI): $m/z = 292$ [$M^+ + 1$].

S-3-Phenyl-propyl N-(4-chlorophenyl)thiocarbamate **4v**. White crystals; mp 85.3–86.0°C; IR (KBr) 1655, 3328 cm^{-1}; ^1H NMR ($CDCl_3$); δ 1.99 (2H, quint, $J = 7.6$ Hz, CH_2), 2.73 (2H, t, $J = 7.6$ Hz, CH_2), 2.98 (2H, t, $J = 7.6$ Hz, CH_2), 7.06 (1H, br s, NH), 7.17–7.37 (9H, m, Ar); ^{13}C NMR ($CDCl_3$); δ 29.7, 31.7, 34.7, 120.8–141.0 (Ar), 165.8; MS (CI): $m/z = 306$ [$M^+ + 1$].

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REFERENCES

[1] (a) Mizuno, T.; Kino, T.; Ito, T.; Miyata, T. Synthetic Commun 2000, 30, 3081–3089; (b) Anbazhagan, M.; Rakeeb, A.; Deshmukh, A. S.; Rajappa, S. Tetrahedron Lett 1998, 39, 3609–3612.

[2] Sitzmann, M. E.; Gilligan, W. H. J Org Chem 1985, 50, 5879–5881.

[3] (a) Quistad, G. B.; Sparks, S. E.; Casida, J. E. Life Sci 1994, 55, 1537–1544; (b) Kochansky, J.; Cohen, C. F. J Agr Entomol 1990, 7, 293–304; (c) Iwata, K.; Yamashita, T.; Uehara, H. Antimicrob Agents Chemother 1989, 33, 2118–2125.

[4] (a) Böhme, A.; Gais, H.-J. Tetrahedron: Asymmetry 1999, 10, 2510–2514; (b) Harayama, H.; Nagahama, T.; Kozera, T.; Kimura, M.; Fugami, K.; Tanaka, S.; Tamaru, Y. Bull Chem Soc Jpn 1997, 70, 445–456; (c) Sakamoto, M.; Yoshiaki, M.; Takahashi, M.; Fujita, T.; Watanabe, S. J Chem Soc, Perkin Trans 1 1995, 373–377.

[5] Riemschneider, R. J Am Chem Soc 1956, 78 844–847.

[6] (a) Mizuno, T.; Nishiguchi, I.; Sonoda, N. Tetrahedron 1994, 50, 5669–5680; (b) Sonoda, N.; Mizuno, T.; Murakami, S.; Kondo, K.; Ogawa, A.; Ryu, I.; Kambe, N. Angewandte Chem 1989, 101, 476–477; (c) Koch, P. Tetrahedron Lett 1975, 2087–2088.

[7] Ishihara, H.; Koketsu, M.; Fukuta, Y.; Nada, F. J Am Chem Soc 2001 123, 8408–8409.

[8] (a) Koketsu, M.; Fukuta, Y.; Ishihara, H. J Org Chem 2002, 67, 1008–1011; (b) Koketsu, M.; Ishida, M.; Takakura, N.; Ishihara, H. J Org Chem 2002, 67, 486–490; (c) Koketsu, M.; Nada, F.; Hiramatsu, S.; Ishihara, H. J Chem Soc, Perkin Trans 1, 2002, 737–740; (d) Koketsu, M.; Takakura, N. Ishihara Synthetic Commun 2002, 32, 3075–3079; (e) Koketsu, M.; Okayama, Y.; Aoki, H.; Ishihara, H. Heteroatom Chem 2002, 13, 195–198; (f) Koketsu, M.; Fukuta, Y.; Ishihara, H. Tetrahedron Lett 2001, 42, 6333–6335.

[9] Preparation of LiAlHSH **2**: To a solution of sulfur powder (0.3 g, 10 mmol) in dry THF (100 ml) was added lithium aluminum hydride (0.38 g, 10.0 mmol) at 0°C under an argon atmosphere. The mixture was stirred for 30 min. The sulfur powder was consumed within 10 min. The reaction mixture became a heterogeneous grayish suspension. The reagent, formed in situ in this way, was used for further reaction.