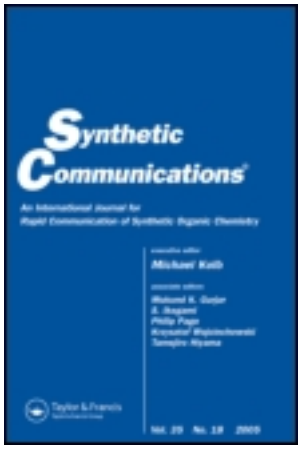

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Stannous Chloride-Promoted Synthesis of S-Allyl-N-aryl Dithiocarbamates under Solvent-Free Conditions

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STANNOUS CHLORIDE–PROMOTED SYNTHESIS OF *S*-ALLYL-*N*-ARYL DITHIOCARBAMATES UNDER SOLVENT-FREE CONDITIONS

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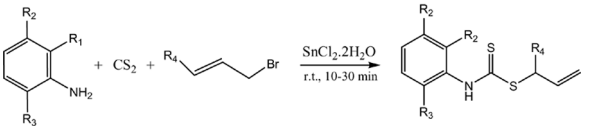
GRAPHICAL ABSTRACT



Abstract *A highly efficient method of synthesis of S-allyl-N-aryl dithiocarbamates using $SnCl_2$ as a catalyst under solvent-free conditions is described. The mild reaction conditions, high yields, and shorter reaction period illustrate the good synthetic utility of this method.*

Keywords Allyl; *N*-aryl dithiocarbamate; $SnCl_2$; solvent-free

INTRODUCTION

Organic dithiocarbamates (dithiourethanes) are biologically important compounds.[1] They are also considered as valuable synthetic intermediates.[2] Because of the ability of dithiocarbamates to chelate with different metal ions, many of the dithiocarbamates have found applications in inorganic analysis.[3] A number of these dithiocarbamates have been used in the rubber industry as vulcanization accelerators.[4] Their applications in the field of agriculture are unlimited.[5] They also possess powerful fungicidal properties.[6] It is therefore of utmost importance that the synthesis of dithiocarbamates should be achieved by a simple and effective method.

Several methods for the synthesis of dithiocarbamate have been reported in the literature, and among them, condensation of primary and secondary amines with costly and toxic reagents, such as thiophosgene and isothiocyanate, constitute the most widely used general methods for the synthesis of this class of compounds.[7] Direct thiocarboxylation of amines with carbon monoxide and sulfur to form urea derivatives has also been reported.[8] Recently, a one-pot reaction of amines with carbonyl sulfide, alkyl halide, or α,β-unsaturated compounds also has been developed.[9] However, these reactions require very toxic reagents and harmful

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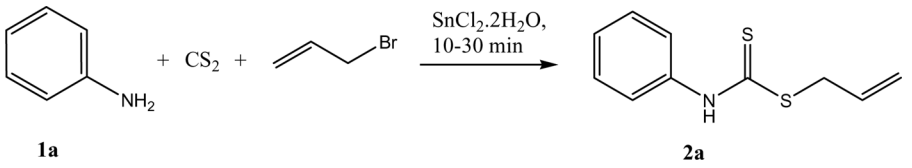


Scheme 1. One-pot, three-component synthesis of *S*-allyl-*N*-aryl-dithiocarbamate **2a**.

organic solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), and methanol in the presence of catalyst.

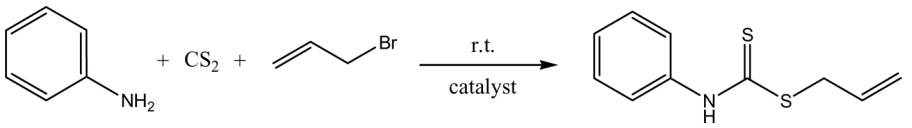
With the increasing interest in developing environmentally benign reactions, organic transformations under solvent-free conditions are ideal processes in organic chemistry. We now report an efficient, novel, and green procedure for the synthesis of sulfur allylated *N*-aryl dithiocarbamates under solvent-free conditions using $SnCl_2 \cdot 2H_2O$ as the catalyst. The methodology represents a one pot, three-component, solvent-free, green synthetic protocol.

Initially, we examined the three-component reaction using aniline (6 mmol), CS_2 (6 mmol), and allylbromide (3 mmol) with $SnCl_2 \cdot 2H_2O$ (0.01 mmol) as catalyst under solvent-free conditions, which afforded the *S*-allylated dithiocarbamate **2a** in 93% yield (Scheme 1).

Next, we evaluated the scope of this catalytic system by employing a wide range of metal salts. The reaction of aniline, CS_2, and allylbromide was carried out as a template using different salts as catalysts. The yields of products under different catalysts are summarized in Table 1. The best yield was obtained using $SnCl_2 \cdot 2H_2O$, and duration of the reaction was only 20 min, whereas in the other catalytic systems the duration for completion was in the range of 3–5 h to get the maximum yield (Table 1).

Thus, we optimized the reaction using $SnCl_2 \cdot 2H_2O$ (0.01 mmol) as the catalyst and stirring the reaction mixture at room temperature for 20 min only. The generality of the present method was extended to different substituted aromatic amines

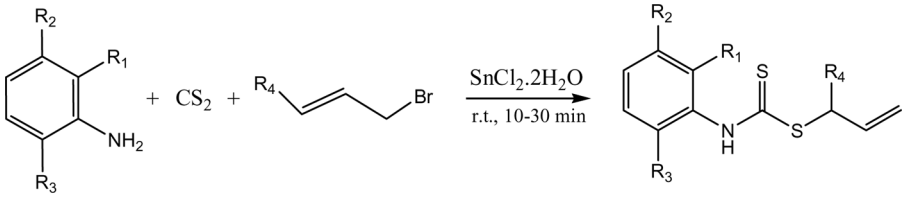
Table 1. Synthesis *S*-allyl-*N*-phenyl dithiocarbamate using different catalysts[a]



Entry	Catalyst	Time	Yield (%)
1	$SnCl_2$	20 min	93
2	$CuCl_2$	3 h	80
3	$FeCl_3$	4 h	81
4	$ZnCl_2$	6 h	70
5	$AlCl_3$	5 h	75

[a]Reaction conditions: solvent-free, aniline (6 mmol), CS_2 (6 mmol), allyl bromide (3 mmol), and catalyst (0.01 mmol).

Table 2. Stannous chloride–promoted allylated dithiocarbamates[a]



1a-i **2a-i**

Entry	R_1	R_2	R_3	R_4	Product	Yield (%)[b]	Mp (°C)
1	H	H	H	H	**2a**	93	185
2	CH_3	H	CH_3	H	**2b**	92	157
3	C_2H_5	H	C_2H_5	H	**2c**	95	145
4	Cl	H	CH_3	H	**2d**	89	163
5	Cl	CH_3	H	H	**2e**	91	201
6	C_2H_5	H	H	H	**2f**	94	115
7	Cl	H	H	H	**2g**	95	215
8	CH_3	H	CH_3	CH_3	**2h**	93	135
9	C_2H_5	H	C_2H_5	CH_3	**2i**	91	115

[a]Reaction conditions: solvent-free, aniline (6 mmol), CS_2 (6 mmol), allyl/crotyl bromide (3 mmol), and catalyst (0.01 mmol).
[b]Isolated yields.

and substituted allyl bromide. As can be seen from Table 2, various substituted anilines, CS_2, and allyl/crotyl bromide were treated under the solvent-free, multi-component reactions to yield the corresponding *S*-allyl-*N*-aryl dithiocarbamates **2a–i** in good to excellent yields.

In summary, we have described a novel, highly efficient, and entirely green protocol for one-pot preparation of *S*-allyl-*N*-aryl dithiocarbamates catalyzed by stannous chloride under solvent-free conditions. The shorter reaction time and good to excellent yield of the desired products are the advantages of this synthetic protocol.

EXPERIMENTAL

Melting points are uncorrected and were determined in capillary tubes on an apparatus containing silicon oil. ^1H and ^{13}C NMR spectra were recorded on a Bruker instrument (AC 300 MHz) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Fourier transform–infrared (FT-IR) spectra were recorded on a Mattson instrument, model Shimadzu IR-408. The microanalyses were performed on a Perkin-Elmer 240B elemental analyzer. Chromatography was performed on SiO_2. The mass spectra were recorded on a Jeol JMSD-300 spectrometer.

General Experimental Procedure for the Preparation of Compound 2a–i

To a mixture of CS_2 (8 mmol) and allyl/crotyl bromide (6 mmol), an aromatic amine (5 mmol) was added in the presence of a catalytic amount of $SnCl_2 \cdot 2H_2O$

(0.5 mmol). The reaction mixture was stirred at room temperature under vigorous magnetic stirring for 10–30 min. Then the organic materials were extracted with chloroform or ethyl acetate (2×10 mL). The combined organic phases were washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated, and white crystals of allylated dithiocarbamates were found at the bottom of the flask. Analytically pure products could be obtained by simple crystallization using either diethyl ether or ethylacetate, and thus column chromatography was not required.

CHARACTERIZATION DATA

S-Allyl-*N*-phenyl Dithiocarbamate (2a)

Mp 185 °C; IR (KBr) (ν max): 1235, 1600, 3137 cm^{-1}, ^1H NMR (DMSO-d_6, 300 MHz) δ 3.91–3.93 (d, $J = 6.2$ Hz, 2H), 5.03, 5.12 (m, 2H), 5.96–6.01 (m, 1H), 6.79–7.01 (m, 5H); ^{13}C NMR (DMSO-d_6, 75.5 MHz) 51.7, 124.3, 126.1, 128.3, 129.1, 133.1, 139.3, 199.9; MS: $m/z = 209$ (M^+). Anal. calcd. for $C_{10}H_{11}NS_2$: C, 57.38; H, 5.30; N, 6.69. Found: C, 57.37; H, 5.33; N, 6.67.

S-Allyl-*N*-(2,6-dimethylphenyl)dithiocarbamate (2b)

Mp 157 °C; IR (KBr) (ν max): 1237, 1569, 3137 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.63 (s, 6H), 4.14–4.15 (d, $J = 6$ Hz, 2H), 5.31–5.33 (m, 2H), 6.05–6.15 (m, 1H), 7.08–7.10 (d, $J = 5.4$ Hz, 2H), 7.18–7.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 19.4, 51.9, 124.5, 126.2, 128.6, 129.3, 131.2, 132.1, 199.5; MS: $m/z =$ 237 (M^+). Anal. calcd. for $C_{12}H_{15}NS_2$: C, 60.72; H, 6.37; N, 5.90. Found: C, 60.71; H, 6.39; N, 5.89.

S-Allyl-*N*-(2,6-diethylphenyl)dithiocarbamate (2c)

Mp 145 °C; IR (KBr) (ν max): 1276, 1573, 3145 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.31–1.35 (t, $J = 9$ Hz, 6H), 3.01–3.03 (d, $J = 6$ Hz, 4H), 4.14–4.16 (d, $J = 5.4$ Hz, 2H), 5.27–5.29 (d, $J = 5.4$ Hz, 2H), 6.04–6.13 (m, 1H), 7.18–7.20 (d, $J = 5.4$ Hz, 2H), 7.31–7.35 (m, 1H), 10.38 (1H, br, NH); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 15.5, 24.8, 53.9, 125.17, 126.75, 127.77, 129.6, 130.0, 138.5, 199.7; MS: $m/z = 265$ (M^+). Anal. calcd. for $C_{14}H_{19}NS_2$: C, 63.35; H, 7.21; N, 5.28. Found: C, 63.51; H, 7.19; N, 5.29.

S-Allyl-*N*-(2-chloro-6-methylphenyl)dithiocarbamate (2d)

Mp 163 °C; IR (KBr) (ν max): 1275, 1579, 3147 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.61 (s, 3H), 4.11–4.15 (d, $J = 5.4$ Hz, 2H), 5.33–5.35 (m, 2H), 6.01–6.13 (m, 1H), 7.29–7.7.39 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 19.1, 51.5, 124.1, 126.5, 128.9, 129.1, 131.7, 132.3, 140.7, 199.9; MS: $m/z = 257$ (M^+). Anal. calcd. for $C_{11}H_{12}NS_2Cl$: C, 51.25; H, 4.69; N, 5.43. Found: C, 51.51; H, 4.19; N, 5.45.

S-Allyl-*N*-(2-chloro-3-methylphenyl)dithiocarbamate (2e)

Mp 201 °C; IR (KBr) (ν max): 1273, 1587, 3149 cm^{-1}; ^1H NMR (DMSO, 300 MHz) δ 2.63 (s, 3H), 4.10–4.23 (d, $J = 5.4$ Hz, 2H), 5.29–5.33 (m, 2H), 6.09–6.15 (m, 1H), 7.19–7.27 (m, 3H); $^{13}CNMR$ (DMSO-d_6, 75.5 MHz) 19.7, 51.3, 124.5, 126.7, 128.3, 129.1, 131.9, 133.1, 140.9, 199.7; MS: $m/z = 257$ (M^+). Anal. calcd. for $C_{11}H_{12}NS_2Cl$: C, 51.25; H, 4.69; N, 5.43. Found: C, 51.33; H, 4.59; N, 5.47.

S-Allyl-*N*-(2-ethylphenyl)dithiocarbamate (2f)

Mp 115 °C; IR (KBr) (ν max): 1275, 1589, 3149 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.31–133 (t, $J = 9$ Hz, 3H), 3.03–3.05 (q, 2H), 4.11–4.14 (d, $J = 5.4$ Hz, 2H), 5.59–6.13 (m, 2H), 6.07–6.11 (m, 1H), 7.29–7.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 15.5, 24.9, 51.5, 125.17, 126.75, 127.77, 129.6, 130.0, 133.1, 136.1, 138.5, 199.7; MS: $m/z = 237$ (M^+). Anal. calcd. for $C_{12}H_{15}NS_2$: C, 60.72; H, 6.37; N, 5.90. Found: C, 60.51; H, 6.19; N, 5.99.

S-Allyl-*N*-(2-chlorophenyl)dithiocarbamate (2g)

Mp 215 °C; IR (KBr) (ν max): 1279, 1587, 3147 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 4.14–4.16 (d, $J = 5.4$ Hz, 2H), 5.27–5.29 (d, $J = 5.4$ Hz, 2H), 6.04–6.13 (m, 1H), 7.18–7.25 (m, 4H), 10.38 (1H, br, NH); ^{13}C NMR (DMSO-d_6, 75.5 MHz) 53.9, 125.1, 126.7, 127.2, 127.9 129.6, 130.0, 136.3, 138.5, 199.9; MS: $m/z = 243$ (M^+). Anal. calcd. for $C_{10}H_{10}NS_2Cl$: C, 49.27; H, 4.13; N, 5.75. Found: C, 49.31; H, 4.19; N, 5.79.

But-3-en-2-yl-(2,6-dimethylphenyl)dithiocarbamate (2h)

Mp 135 °C; IR (KBr) (ν max): 1275, 1589, 3145 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.62–1.63 (d, $J = 4.2$ Hz, 3H), 2.64–2.68 (s, 6H), 4.07–4.09 (d, $J = 5.1$ Hz, 2H), 5.03–5.12 (m, 1H), 5.65–5.80 (m, 1H), 7.07–7.09 (d, $J = 5.7$ Hz, 2H), 7.17–7.27 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 17.8, 19.8, 52.1, 119.5, 129.2, 129.9, 131.8, 132.9, 137.5, 199.7; MS: $m/z = 251$ (M^+). Anal. calcd. for $C_{13}H_{17}NS_2$: C, 62.11; H, 6.82; N, 5.57. Found: C, 62.51; H, 6.79; N, 5.59.

But-3-en-2-yl-(2,6-diethylphenyl)dithiocarbamate (2i)

Mp 115 °C; IR (KBr) (ν max): 1269, 1591, 3153 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.31–1.35 (t, $J = 7.5$ Hz, 6H), 1.61–1.63 (d, $J = 4.2$ Hz, 3H), 3.01–3.03 (d, $J = 6$ Hz, 4H), 4.14–4.16 (m, 1H), 5.27–5.29 (m, 2H), 6.04–6.13 (m, 1H), 7.18–7.20 (d, $J = 5.4$ Hz, 2H), 7.31–7.35 (m, 1H), 10.38 (1H, br, NH); ^{13}C NMR ($CDCl_3$, 75.5 MHz) 17.5, 19.3, 24.8, 53.9, 119.5, 129.5, 129.9, 131.7, 132.9, 137.9, 199.7; MS: $m/z = 279$ (M^+). Anal. calcd. for $C_{15}H_{21}NS_2$: C, 64.47; H, 7.57; N, 5.01. Found: C, 64.51; H, 7.59; N, 5.09.

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