Palladium-Catalyzed Syntheses of 2-Arylbenzothiazoles

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A new method is described for the synthesis of 2-arylbenzothiazoles which consists of reacting a haloaromatic compound with an *o*-aminothiophenol in the presence of 95 psig of carbon monoxide (CO), a palladium catalyst, and 2,6-lutidine in DMAc. Choice of base is critical to suppress unwanted side reactions that give amide thioesters, dimethylbenzamides, and 2-methylbenzothiazoles. This method is tolerant of a variety of functional groups and offers a route to 2-arylbenzothiazoles complementary to those that conventionally employ acid chlorides.

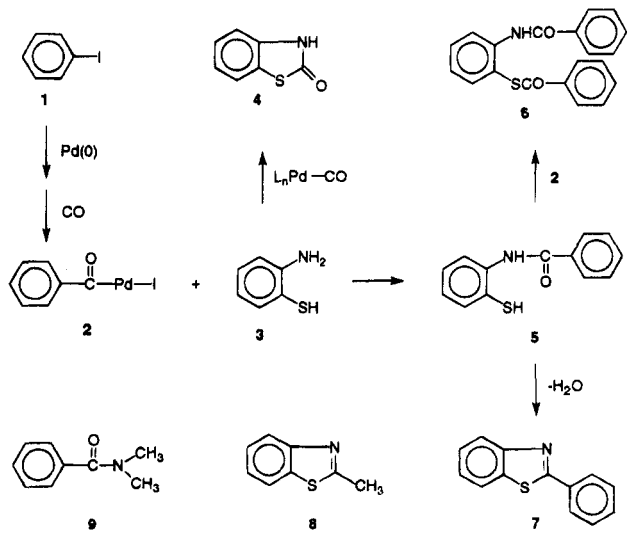
Introduction

We recently reported a new synthetic route to benzoxazoles and benzimidazoles based on a palladium-catalyzed carbonylation and condensation reaction.[1,2] In an effort to extend this chemistry to benzothiazoles, the reactions of *o*-aminothiophenols and haloaromatics were explored. The benzothiazole nucleus is a key element in some thermally stable rigid-rod polymers possessing high tensile strength and modulus[3] as well as a number of pharmacologically active compounds.[4] We herein report the initial results of our investigation.

Results and Discussion

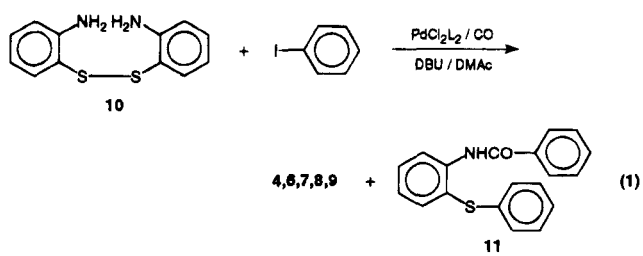
The reaction of *o*-aminothiophenol, iodobenzene, and CO under conditions found favorable for benzoxazole formation[1] (*N*,*N*-dimethylacetamide, DMAc, at 115 °C, with 1.2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1.5% $PdCl_2L_2$ catalyst, where L = PPh_3) resulted in the formation of a variety of products (Scheme 1). Only a small amount of the desired 2-phenylbenzothiazole (**7**) was formed. The major products of the reaction were 2-methylbenzothiazole (**8**) and *N*,*N*-dimethylbenzamide (**9**), with some 2-benzothiazolone (**4**) and a trace of amide thioester (**6**). Compound **4** was formed by attack of *o*-aminothiophenol on CO.[5] The desired product **7** and amide thioester **6** likely arose from the common intermediate **5**. Compound **6** may be

Scheme 1



the result of the comparable nucleophilicities of both the amino and thiol functionalities under these conditions. None of the suspected intermediate *N*-(2-mercaptophenyl)benzamide (**5**) was observed.

Use of disulfide **10** as a means to decrease the reactivity of the thiol group resulted in the same byproducts being formed as well as the amide sulfide **11** (eq 1).



(1)

To decrease the side reactions, our attention focused on the base. In benzimidazole formation, we found that strong amine bases, such as DBU, promoted intermolecular bis(amide) formation over intramolecular cyclization.[2] Use of a weaker base, such as 2,6-lutidine, enhanced the desired cyclization reaction. Examination of the *o*-aminothiophenol reaction using bases with a pK_a range of 4.9–11.9 revealed that most of the iodo-

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(1) Perry, R. J.; Wilson, B. D.; Miller, R. J. *J. Org. Chem.* **1992,** *57,* 2883.

(2) Perry, R. J.; Wilson, B. D. *J. Org. Chem.* **1993,** *58,* 7016.

(3) (a) Hergenrother, P. M.; Wrasildo, W.; Levine, H. H. *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* **1964,** *5,* 153. (b) Imai, Y.; Taoka, I.; Uno, K.; Iwakura, Y. *Makromol. Chem.* **1965,** *83,* 167. (c) Cassidy, P. E. In *Thermally Stable Polymers*; Marcel Dekker: New York, 1980. (d) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules* **1981,** *14,* 915. (e) Allen, S. R.; Filippov, A. G.; Farris, R. J.; Thomas, E. L.; Wong, C. P.; Berry, G. C.; Chenevey, E. C. *Macromolecules* **1981,** *14,* 1135. (f) Ueda, M.; Yokote, S.; Sato, M. *Polym. J.* **1986,** *18,* 117. (g) Feldman, L.; Farris, R. J.; Thomas, E. L. *J. Mater. Sci.* **1985,** *20,* 2719, 2727, 4583. (h) Hattori, T.; Akita, H.; Kakimoto, M.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1992,** *30,* 197.

(4) Campbell, M. M. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 4, p 993.

(5) The CO may be bound to the metal, although that is not necessary for carbonylation to occur in some instances. See: (a) Toshiyuki, M.; Kanbe, N.; Murai, S.; Sonoda, N.; Nishiguchi, I.; Hirashima, T. *Nippon Kagaku Kaishi* **1987,** 1332. (b) Bassoli, A.; Rindone, B.; Tollari, S.; Chioccara, F. *J. Mol. Catal.* **1990,** *60,* 41. (c) Drent, E. Eur. Pat. Appl. 255744 to Shell Internationale Research Maatschappij BV, Feb 10, 1988.

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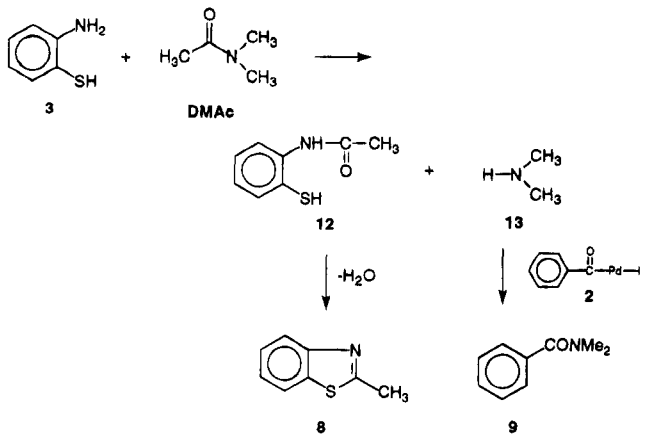
Scheme 2



benzene was still present after 24 h when quinoline (pK_a = 4.9) was used and a large fraction remained in the presence of pyridine (pK_a = 5.2). On the other hand, strong bases, such as DBU (pK_a = 11.9) and 1,4-diazabicyclo[2.2.2]octane (DABCO; pK_a = 8.2), showed no starting material present but permitted the formation of large amounts of 2-methylbenzothiazole (**8**) and *N,N*-dimethylbenzamide (**9**). Modest bases substantially decreased these undesired byproducts, although they did not completely suppress them. Of the latter bases, 2,6-lutidine (pK_a = 6.8) and 4-picoline (pK_a = 6.0) gave the cleanest reaction as seen by gas chromatography (GC), and an 87% yield of product was isolated when 2,6-lutidine was used as the base.

We believed that **8** and **9** were formed by palladium-assisted solvent decomposition, as was seen in benzimidazole formation.[2] However, control experiments indicated that Pd was not necessary for the formation of **8**. When *o*-aminothiophenol was heated with DMAc at 110 °C for 18 h, a large amount of **8** was detected. Direct attack of **3** on DMAc could generate **12** and liberate dimethylamine (**13**). The likely source of **9** was then from the reaction of the liberated dimethylamine with aroylpalladium species (**2**) (Scheme 2). Chlorobenzene and diglyme were also examined as solvents, as they would be unable to dissociate and react with *o*-aminothiophenol or the palladium acyl complex. In both cases, substantial amounts of starting materials remained after 24 h.

To determine why the stronger bases resulted in more side-product formation, a series of reactions were run in which DMAc and benzoyl chloride were heated together with no base present and with either DBU or 2,6-lutidine. Any dimethylamino fragments formed from DMAc dissociation would be trapped by benzoyl chloride to generate **9**. In the control reaction with just DMAc and benzoyl chloride, we found some formation of *N,N*-dimethylbenzamide (**9**). When 2,6-lutidine was present, substantially more **9** was formed. In the reaction with DBU, nearly twice the amount of **9** was produced compared to the lutidine reaction. This indicated that the stronger base caused more solvent decomposition which, in turn, generated products **8** and **9**. The weaker base 2,6-lutidine was not as efficient at solvent dissociation and therefore allowed the desired amidation reaction to occur to a much greater extent.

(6) Brembilla, A.; Lochon, P. *C.R. Seances Acad. Sci. Ser. C* **1978**, *286*, 557.
(7) Cohen, V. I. *J. Heterocycl. Chem.* **1979**, *16*, 13.

Using the best conditions reported above, we wished to determine the scope of this reaction. Table 1 shows that good yields of the desired 2-arylbenzothiazoles can be formed from both iodo- and bromoaromatics and *o*-aminothiophenol. Electron-donating and -withdrawing groups as well as heteroaromatic groups are tolerated in this reaction. In all cases, detectable amounts of 2-methylbenzothiazole, 2-benzothiazolone, and the corresponding *N,N*-dimethyl amides were formed. These could not be completely suppressed and constituted 5–20% of the reaction products. These byproducts were easily removed by chromatography through a short silica gel column. When substituted *o*-aminothiophenols were allowed to react with iodobenzene (Table 2), substantially greater yields of the desired benzothiazoles were obtained with substituents in the 5-position as compared to the 6-position. The reason for this is unclear at present.

Conclusion

We have demonstrated a new synthetic route for the preparation of 2-arylbenzothiazoles from *o*-aminothiophenols, aryl halides, and CO. Good yields of products can be obtained through the proper choice of base, which suppresses unwanted amide thioester as well as benzamide and 2-methylbenzothiazole formation. A variety of substituents on both the haloaromatic moiety or the *o*-aminothiophenol unit are tolerated.

Experimental Section

General Procedures. Reactions were performed in a 120-mL pressure reaction vessel (containing a stirbar) from Aerosol Laboratory Equipment Corp. fitted with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawal. All reactions were run at 0.33 M in *N,N*-dimethylacetamide (DMAc) at 110–115 °C under 95 psig of CO using 1.5% $PdCl_2L_2$ as the catalyst system unless otherwise noted.

All reactions were monitored on an HP 5890 gas chromatograph using a 15-m, 0.25-μm DB-5 column (0.32 mm i.d.) and a flame ionization detector. Helium flow rate through the column was 4.0 mL/min. The GC parameters employed for analysis were as follows: injection port, 300 °C; detector, 350 °C; temperature ramp from 50 °C (hold 1 min) to 300 °C (hold 10 min) at 20 °C/min. Proton NMR spectra and ^{13}C NMR spectra were recorded on a General Electric QE-300 (300 MHz) spectrometer using DMSO-d_6 as solvent and internal standard. Fourier transform infrared spectra were recorded on a Nicolet 60SX spectrometer as KBr pellets. Chromatography was performed using Woelm 60–200 mesh silica gel. Elemental analyses were performed by the Analytical Technology Division of Eastman Kodak Co.

Chemicals. DMAc (anhydrous), iodobenzene, 4-iodotoluene, 4-bromotoluene, 4-iodoanisole, 1-chloro-4-iodobenzene, 4'-bromoacetophenone, 4'-iodoacetophenone, 4-iodobenzonitrile, 4-iodobiphenyl, 4-iodobenzoic acid, 2-iodothiophene, 2-bromopyridine, CO (UPC grade), bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$), 2-amino-4-chlorothiophenol hydrochloride, *p*-toluidine, *p*-chloroaniline, 2,5-dimethylbenzo-

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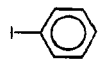
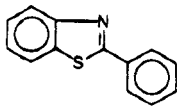
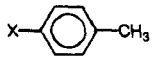
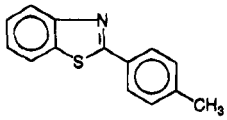
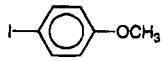
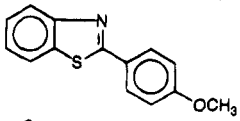
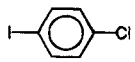
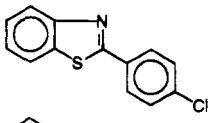
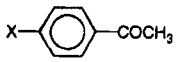
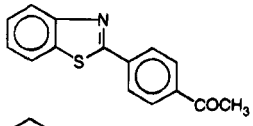
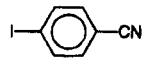
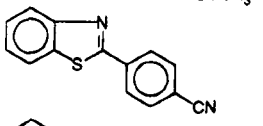
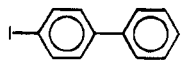
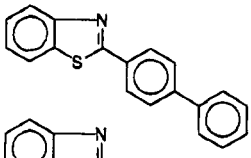
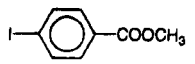
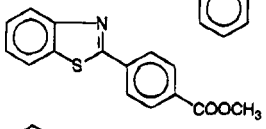
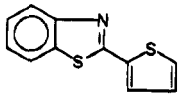
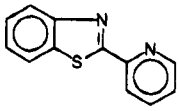
(10) Wattenberg, L. W.; Page, M. A.; Leong, J. L. *Cancer Res.* **1968**, *28*, 2539.
(11) Kuhlmann, U.S. Patent 2,195,011, 1938; Beilstein 4-27-00-01399.
(12) El-Meligy, Von M. S. A.; Mohamed, S. A. *J. Prakt. Chem.* **1974**, *316*, 154.

Table 1. Reactions of *o*-Aminothiophenol with Substituted Haloaromatics[a]

compd	haloaromatic	benzothiazole 7	mp (°C)[b] (recrystallizn solvent)	yield (%)[c]
a			113 - 113.5 [d] (2:1 EtOH/H_2O)	87
b			85 - 85.5 [e] (2:1 EtOH/H_2O)	X = I 82 X = Br 88
c			121.5 - 122 [f] (2:1 EtOH/H_2O)	81
d			116 - 116.5 [g] (EtOH)	88
e			182 - 183 [h] (5:2 EtOH/toluene)	X = I 67 X = Br 41
f			166.5 - 167.5 [i] (3:2 EtOH/toluene)	62
g			205.5 - 206.5 [j] (5:3 EtOH/toluene)	78
h			166 - 166.5 [k] (5:2 MeOH/toluene)	93
i			98 - 98.5 [l] (2:1 MeOH/H_2O)	64
j			132.5 - 133 [m] (heptane)	68

[a] Conditions: reaction in DMAc (0.33 M), 110 °C, 95 psig of CO, 1.5% $PdCl_2L_2$, 1.2 equiv of 2,6-lutidine, 24 h. [b] Uncorrected. [c] Yields of isolated, purified products. [d] Lit.[6] mp 114 °C. [e] Lit.[6] mp 86 °C. [f] Lit.[8] mp 121–122 °C. [g] Lit.[7] mp 116.5 °C. [h] Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53; S, 12.66. Found: C, 71.31; H, 4.30; N, 5.44. [i] Lit.[6] mp 171 °C. [j] Lit.[6] mp 209 °C. [k] Lit.[9] mp 164 °C. [l] Lit.[7] mp 98 °C. [m] Lit.[7] mp 132 °C.

thiazole, NaSCN, sulfuryl chloride, ethylene glycol, *p*-toluenesulfonic acid hydrate (*p*-TsOH·H_2O), concentrated H_2SO_4, KOH, $NaBH_4$, and 2-amino-4-(trifluoromethyl)thiophenol hydrochloride were all purchased from commercial suppliers and used as received. DBU, 2,6-lutidine, *s*-collidine, pyridine, quinoline, and *o*-aminothiophenol were all purchased from commercial suppliers and fractionally distilled before use.

The *p*-toluenesulfonic acid salts of 2-amino-4-methylthiophenol, 2-amino-5-methylthiophenol, and 2-amino-5-chlorothiophenol were synthesized as described below. 2,2′-Diaminodiphenyl disulfide was prepared by the oxidative coupling of o-aminothiophenol in DMSO.[13]

Preparation of Starting Materials. 2-Amino-4-methylthiophenol–*p*-Toluenesulfonic Acid. A mixture of 2,5-dimethylbenzothiazole (25.0 g, 150 mmol), KOH (43 g, 766 mmol), water (20 mL), ethylene glycol (60 mL), and $NaBH_4$ (4.8 g, 127 mmol) were refluxed for 2 h, after which time additional $NaBH_4$ (1.0 g, 26 mmol) was added. The mixture was cooled, neutralized to pH 7 with $NaHCO_3$-buffered AcOH, and then extracted with CH_2Cl_2. The organic extracts were washed with water, dried over $MgSO_4$, and then treated with *p*-TsOH·H_2O (30.4 g, 160 mmol). The salt, which precipitated, was washed with CH_2Cl_2 to give 24.7 g (53%) of the product. ^1H NMR (DMSO-d_6): δ 7.70 (br s, 4), 7.50 (d, J = 8.0 Hz, 2), 7.14 (d, J = 7.9 Hz, 1), 7.10 (d, J = 8.0 Hz, 2), 7.03 (d, J = 2.0 Hz, 1), 6.85 (dd, J = 8.0, 2.0 Hz, 1), 2.24 (s, 3), 2.22 (s, 3). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 144.8, 141.6, 138.9, 138.4, 135.0, 128.4, 125.6, 125.4, 121.9, 121.7, 20.9. Anal. Calcd for $C_{14}H_{17}NO_3S_2$: C, 54.00; H, 5.50; N, 4.50; S, 20.59. Found: C, 54.08; H, 5.42; N, 4.38; S, 20.78.

2-Amino-5-methylthiophenol–*p*-Toluenesulfonic Acid. Following the method of Allen and Van Allan,[14] H_2SO_4 (54 g) was added to a solution of *p*-toluidine (107 g, 0.79 mol) in chlorobenzene (700 mL). This mixture was teated with NaSCN (90 g, 1.11 mol) and heated to 100 °C for 3 h. The solution was cooled to 30 °C, and sulfuryl chloride (180 g, 1.33 mol) was added while the reaction temperature was kept below

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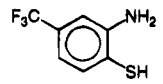
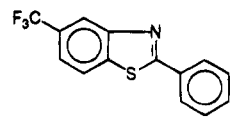
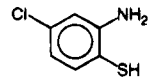
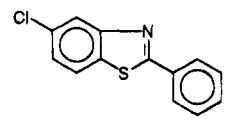
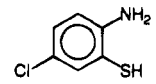
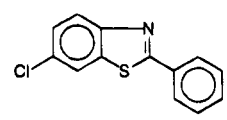
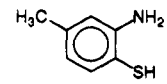
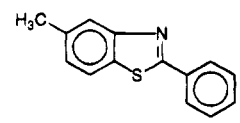
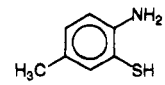
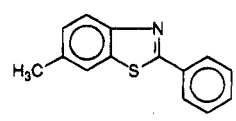
(14) Allen, C. F. H.; Van Allan, J. In *Organic Syntheses*; Horning, E. C., Ed.; Wiley: New York, 1964; Collect. Vol. III, p 76.

Table 2. Reactions of *o*-Aminothiophenols with Iodobenzene[a]

compd	*o*-aminothiophenol	benzothiazole 7	mp (°C)[b] (recrystallizn solvent)	yield (%)[c]
k			132 - 132.5 [d] (3:1 EtOH/H_2O)	48
l			139 -139.5 [e] (EtOH)	83
m			156.5 - 157 [f] (5:1 EtOH/H_2O)	23
n			150.5 - 151 [g] (EtOH)	81
o			123 - 123.5 [h] (1:1 EtOH/H_2O)	33

[a] Conditions: reaction in DMAc (0.33 M), 110 °C, 95 psig of CO, 1.5% $PdCl_2L_2$, 1.2 equiv of 2,6-lutidine, 24 h. [b] Uncorrected. [c] Yields of isolated, purified products. [d] Anal. Calcd for $C_{14}H_8F_3NS$: C, 60.21; H, 2.89; F, 20.41; N, 5.02; S, 11.48. Found: C, 59.97; H, 2.85; N, 5.11. [e] Lit.[10] mp 139–141 °C. [f] Lit.[11] mp 148 °C. [g] Lit.[12] mp 156–157 °C. [h] Lit.[10] mp 125–125.5 °C.

50 °C. The reaction mixture was stirred for 7 h and then allowed to stand overnight. The solid which formed was collected by filtration, dissolved in water, and made basic with NH_4OH. The 2-amino-6-methylbenzothiazole was collected by filtration, washed with water, and recrystallized once from 95% ethanol to give 54 g (42%) of the intermediate. The intermediate (25 g, 0.15 mol) was added to 500 mL of aqueous KOH (25 g of KOH, 0.45 mol), and this mixture was refluxed for 3 days. The reaction mixture was cooled and treated with 6 N HCl to pH 8; then *p*-TsOH·H_2O (35 g, 0.18 mol) was added and the resulting mixture concentrated in vacuo. The residue was extracted with EtOAc, and the extract was filtered and placed in a freezer. The product (7.0 g, 15%) crystallized on cooling. ^{1}H NMR (DMSO-d_6): δ 7.62 (br s, 4), 7.48 (d, J = 8.0 Hz, 2), 7.21 (s, 2), 7.09 (m, 3), 2.25 (s, 3), 2.17 (s 3). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 144.9, 138.2, 135.1, 134.9, 134.7, 131.8, 128.3, 126.0, 125.6, 122.0, 20.9, 20.2. Anal. Calcd for $C_{14}H_{17}NO_3S_2$: C, 54.00; H, 5.50; N, 4.50; S, 20.59. Found: C, 53.84; H, 5.58; N, 4.239; S, 20.71.

2-Amino-5-chlorothiophenol–*p*-Toluenesulfonic Acid. This compound was made by the method described above using *p*-chloroaniline (127 g, 1.0 mol), chlorobenzene (700 mL), H_2SO_4 (54 g), and NaSCN (90 g, 1.11 mol). The intermediate was obtained in 34% yield. The intermediate (35 g, 0.19 mol) was then treated as above to give 12 g (19%) of the product. ^{1}H NMR (DMSO-d_6): δ 7.74 (br s, 4), 7.50 (d, J = 7.9 Hz, 2), 7.25 (dd, J = 8.7, 2.0 Hz, 1), 7.10 (d, J = 8.0 Hz, 2), 7.08 (m, 1), 7.02 (d, J = 8.7 Hz, 1), 2.24 (s, 3). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 144.5, 143.0, 138.7, 133.6, 131.1, 128.5, 125.7, 123.7, 122.3, 120.0, 21.0. Anal. Calcd for $C_{13}H_{14}ClNO_3S_2$: C, 47.05; H, 4.25; N, 4.22; Cl, 10.68; S, 19.32. Found: C, 46.96; H, 4.27; N, 4.39; S, 19.47.

Detailed Example. Preparation of 2-(4-Acetylphenyl)-benzothiazole (7e). A pressure vessel was charged with *o*-aminothiophenol (1.00 mL, 9.35 mmol), iodoacetophenone (2.301 g, 9.35 mmol), $PdCl_2L_2$ (98 mg, 0.14 mmol), and DMAc (28 mL). The contents were deoxygenated with argon and then placed under 15 psig of CO and stirred at 110 °C until all reagents had dissolved. Then the pressure was released and 2,6-lutidine (1.31 mL, 11.2 mmol) was added by syringe through the ball valve. The reactor was charged to 95 psig of CO and stirred for 24 h at 110 °C. The reaction mixture was filtered through filter-aid to remove palladium and then concentrated in vacuo. The residue was dissolved in a hot toluene/methylene chloride mixture and chromatographed on a short (5 cm) silica gel column, with toluene as eluent. The appropriate fractions were collected and recrystallized twice from 5:2 ethanol/toluene to give 1.60 g (67%) of the product as off-white crystals, mp 182–183 °C. Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53; S, 12.66. Found: C, 71.31; H, 4.30; N, 5.44.

Spectral characteristics of the isolated benzothiazoles are given below.

2-Phenylbenzothiazole (7a). ^{1}H NMR (DMSO-d_6): δ 8.06 (m, 4), 7.52 (m, 4), 7.41 (t, J = 7.5 Hz, 1). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 167.2, 153.5; 134.4, 132.8, 131.3, 129.3, 127.1, 126.6, 125.5, 122.8, 122.2. FTIR (KBr): 3064, 1606, 1478, 1433, 1314, 1225, 1071, 963, 760, 688, 624 cm^{-1}.

2-(4-Methylphenyl)benzothiazole (7b). ^{1}H NMR (DMSO-d_6): δ 8.02 (m, 2), 7.90 (d, J = 8.1 Hz, 2), 7.49 (t, J = 7.3 Hz, 1), 7.39 (t, J = 7.3 Hz, 1), 7.27 (d, J = 8.0 Hz, 2), 2.31 (s, 3). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 167.3, 153.6, 141.3, 134.3, 130.2, 129.8, 127.0, 126.5, 125.2, 122.7, 122.1, 21.0. FTIR (KBr): 3034, 2935, 1608, 1484, 1434, 1312, 1182, 960, 818, 762, 731, 623 cm^{-1}.

2-(4-Methoxyphenyl)benzothiazole (7c). ^{1}H NMR (DMSO-d_6): δ 8.05 (m, 2), 7.97 (d, J = 8.6 Hz, 2), 7.48 (t, J = 7.5 Hz, 1), 7.38 (t, J = 7.6 Hz, 1), 7.07 (d, J = 8.8 Hz, 2), 3.81 (s, 3). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 167.0, 161.7, 153.6, 134.2, 128.8, 126.4, 125.5, 125.0, 122.4, 122.1, 114.7, 55.4. FTIR (KBr): 3060, 2992, 2835, 1605, 1522, 1485, 1434, 1310, 1260, 1226, 1172, 1028, 969, 833, 760, 692, 629 cm^{-1}.

2-(4-Chlorophenyl)benzothiazole (7d). ^{1}H NMR (DMSO-d_6): δ 8.08 (m, 2), 8.06 (d, J = 8.5 Hz, 2), 7.59 (d, J = 8.5 Hz, 2), 7.52 (t, J = 7.6 Hz, 1), 7.44 (t, J = 7.6 Hz, 1). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 165.9, 153.4, 136.0, 134.5, 131.6, 129.4, 128.8, 126.7, 125.7, 122.9, 122.4. FTIR (KBr): 3054, 1589, 1474, 1399, 1314, 1251, 1090, 1013, 966, 829, 756, 692 cm^{-1}.

2-(4-Acetylphenyl)benzothiazole (7e). ^{1}H NMR (DMF-d_7): δ 8.30 (d, J = 8.4 Hz, 2), 8.19 (d, J = 8.4 Hz, 2), 8.18 (m, 2), 7.63 (dt, J = 8.4, 1.1 Hz, 1), 7.54 (dt, J = 8.1, 1.0 Hz, 1), 2.70 (s, 3). ^{13}C{^{1}H} NMR (DMF-d_7): δ 197.9, 154.7, 139.6, 137.7, 135.9, 129.8, 128.2, 127.6, 126.7, 124.0, 123.1, 109.0, 27.0. FTIR (KBr): 3061, 2995, 1679, 1600, 1476, 1433, 1355, 1267, 971, 828, 767, 620 cm^{-1}.

2-(4-Cyanophenyl)benzothiazole (7f). ^{1}H NMR (DMSO-d_6): δ 8.21 (d, J = 8.2 Hz, 2), 8.16 (d, J = 7.9 Hz, 1), 8.08 (d, J = 8.1 Hz, 1), 7.99 (d, J = 8.4 Hz, 1), 7.51 (m, 2). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 165.3, 153.4, 136.6, 134.9, 133.3, 127.8, 127.0, 126.2, 123.3, 122.6, 118.3, 113.3. FTIR (KBr): 3054, 2228, 1605, 1481, 1433, 1315, 1251, 968, 841, 722, 695, 617 cm^{-1}.

2-(4-Biphenyl)benzothiazole (7g). ^{1}H NMR (DMSO-d_6): δ 8.14 (m, 3), 8.05 (d, J = 7.9 Hz, 1), 7.86 (d, J = 8.3 Hz, 2), 7.74 (d, J = 7.4 Hz, 2), 7.48 (m, 5). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 166.8, 153.6, 142.8, 138.9, 134.4, 131.8, 129.1, 128.2, 127.8, 127.5, 126.8, 126.7, 125.6, 122.9, 122.4. FTIR (KBr): 3022, 1560, 1478, 1435, 1404, 1315, 1253, 967, 841, 757, 729, 720, 688 cm^{-1}.

2-(4-(Methoxycarbonyl)phenyl)benzothiazole (7h). ^{1}H NMR (DMSO-d_6): δ 8.20 (m, 3), 8.11 (m, 3), 7.56 (t, J = 7.4 Hz, 1), 7.49 (t, J = 7.4 Hz, 1), 3.87 (s, 3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 165.9, 165.5, 153.5, 136.7, 134.7, 131.6, 130.1, 127.4, 126.9, 126.0, 123.2, 122.5, 52.4. FTIR (KBr): 2940, 1715, 1607, 1478, 1434, 1280, 1108, 967, 861, 772, 762, 693 cm^{-1}.

2-(2-Thienyl)benzothiazole (7i). ^{1}H NMR (DMSO-d_6): δ 8.03 (d, J = 7.9 Hz, 1), 7.96 (d, J = 8.0 Hz, 1), 7.81 (d, J = 5.1 Hz, 1), 7.76 (d, J = 3.4 Hz, 1), 7.48 (t, J = 7.4 Hz, 1), 7.38 (t, J = 7.7 Hz, 1), 7.18 (t, J = 4.3 Hz, 1). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 160.8, 153.0, 136.3, 134.2, 130.7, 129.5, 128.6, 126.6, 125.4, 122.4, 122.2. FTIR (KBr): 3058, 1541, 1474, 1434, 1416, 1312, 1223, 1078, 912, 827, 761, 714 cm^{-1}.

2-(2-Pyridyl)benzothiazole (7j). ^{1}H NMR (DMSO-d_6): δ 8.68 (d, J = 4.4 Hz, 1), 8.28 (d, J = 7.9 Hz, 1), 8.11 (d, J = 7.7 Hz, 1), 8.06 (d, J = 8.0 Hz, 1), 7.99 (t, J = 7.3 Hz, 1), 7.52 (m, 2), 7.45 (t, J = 7.3 Hz, 1). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 169.0, 153.7, 150.3, 149.9, 137.8, 135.4, 126.5, 126.0, 125.9, 123.2, 122.5, 120.3. FTIR (KBr): 3060, 1584, 1564, 1509, 1456, 1433, 1316, 1267, 996, 979, 783, 759, 740 cm^{-1}.

2-Phenyl-5-(trifluoromethyl)benzothiazole (7k). ^{1}H NMR (DMSO-d_6): δ 8.38 (d, J = 7.2 Hz, 2), 8.09 (d, J = 7.5 Hz, 2), 7.75 (d, J = 8.5 Hz, 1), 7.59 (m, 3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 170.0, 153.1, 138.6, 132.3, 132.0, 129.5, 127.4, 126.0, 123.9, 122.4, 121.5, 119.6. FTIR (KBr) 3040, 1481, 1419, 1331, 1321, 1257, 1173, 1144, 1110, 1074, 1054, 966, 899, 825, 768 cm^{-1}.

2-Phenyl-5-chlorobenzothiazole (7l). ^{1}H NMR (DMSO-d_6): δ 8.15 (d, J = 8.6 Hz, 1), 8.08 (dd, J = 10.8, 1.6 Hz, 1), 8.05, (m, 1), 7.56 (m, 3), 7.47 (dd, J = 8.5, 1.7 Hz, 1). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 169.6, 154.4, 133.2, 132.5, 131.8, 131.4, 129.4, 127.3, 125.6, 123.9, 122.2. FTIR (KBr): 3077, 1585, 1543, 1477, 1432, 1263, 1226, 1063, 968, 883, 807, 764, 688, 628 cm^{-1}.

2-Phenyl-6-chlorobenzothiazole (7m). ^{1}H NMR (DMSO-d_6): δ 8.27 (m, 1), 8.04 (m, 3), 8.05 (m, 1), 7.55 (m, 4). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 168.1, 152.3, 136.0, 132.5, 131.7, 130.0, 129.4, 127.2, 127.1, 124.0, 122.0. FTIR (KBr): 3060, 1587, 1544, 1510, 1479, 1438, 1306, 1246, 1224, 1105, 969, 865, 820, 764, 759, 684 cm^{-1}.

2-Phenyl-5-methylbenzothiazole (7n). ^{1}H NMR (DMSO-d_6): δ 8.09 (m, 2), 7.90 (br s, 1), 7.76 (d, J = 8.2 Hz, 1), 7.48 (m, 3), 7.22 (d, J = 8.0 Hz, 1), 2.52 (s, 3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 168.0, 154.5, 136.3, 133.7, 132.0, 130.7, 128.9, 127.4, 126.7, 123.2, 121.0, 21.4. FTIR (KBr) 3064, 2940, 1605, 1477, 1441, 1315, 1233, 1072, 967, 876, 808, 771, 692, 628 cm^{-1}.

2-Phenyl-6-methylbenzothiazole (7o). ^{1}H NMR (DMSO-d_6): δ 8.03 (m, 2), 7.90 (d, J = 8.4 Hz, 1), 7.86 (br s, 1), 7.53 (m, 3), 7.32 (d, J = 8.3 Hz, 1), 2.41 (s, 3). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 166.1, 151.7, 135.3, 134.6, 133.0, 131.2, 129.3, 128.1, 127.0, 122.4, 121.8, 21.0. FTIR (KBr): 3020, 2920, 1509, 1480, 1441, 1313, 1257, 970, 816, 767, 691 cm^{-1}.

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