Reactions of Benzyl Aryl Sulfides with Excess Active Halogen Reagents

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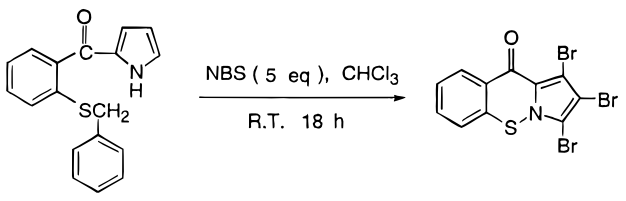
1,2,3-Tribromopyrrolo[1,2-*b*][1,2]benzothiazin-10-one (**2**) is produced from 2-[2-(benzylthio)benzoyl]-pyrrole (**1**) when treated with excess (5 equiv) NBS in $CHCl_3$. With NCS, a mixture is obtained in which di- and trichloropyrrolo[1,2-*b*][1,2]benzothiazin-10-ones are present. If ethanol is present in the NCS reaction, compound **4** is formed as the major product. Further, compound **3** is also formed by the reaction of compound **1** or the corresponding disulfide with excess $SOCl_2$. A novel route to alkyl arenesulfinic esters is also reported. Treatment of a benzyl aryl sulfide with excess (5 equiv) NCS in the presence of an *n*-alkyl alcohol (7 equiv) produces an *n*-alkyl arenesulfinic ester in good yield. An arenesulfonyl chloride is the major product in the presence of benzyl alcohol.

Introduction

Intramolecular sulfoxide electrophilic sulfenylation (SES) reactions have been used extensively in our laboratory to generate sulfur-bridged heterocyclic compounds.[1,2] These reactions are often conducted by simply refluxing the sulfoxide in *p*-xylene, producing the product and a low molecular weight alcohol (methanol or ethanol, typically) as the sole byproduct. The more traditional reagents for intermolecular sulfenylation involve active halogen species which we felt would react competitively with the electron rich aromatic ring present in our starting materials. However, the antibiotic activity of halogenated pyrroles such as pyrrolnitrin,[3] pyoluteorin,[4] and pentabromopseudilin[5,6] has led us to investigate the reaction of suitably substituted sulfides with active halogen reagents. Previous work on the reaction of active halogen reagents with organic sulfides suggests three paths may result as follows: benzylic C−S bond cleavage in benzylic sulfides, attack at sulfur followed by Pummerer-type chemistry, or attack at sulfur followed by displacement at sulfur by a nucleophile or rich π-electron source. Chlorine,[7] Br_2,[8] and SO_2Cl_2[8,9] convert benzyl sulfides into sulfenyl halides with elimination of benzyl chloride. NCS and NBS in aprotic solvents (CCl_4 or $CHCl_3$) have been found to promote Pummerer-type reactions in which α-chloro sulfides are formed.[10] Similar results are found with *tert*-butyl hypochlorite.[11] Finally, Muchowski and others have used dimethyl succinimidosulfonium chloride (dimethyl sulfide/NCS) extensively for pyrrole methylsulfenylation.[12] Since we were interested in promoting pyrrole sulfenylation in our systems, NCS and NBS seemed to be appropriate reagents for halogen-promoted cyclization of substrates such as **1**. In this paper, we wish to report some reactions of **1** and other benzyl aryl sulfides with these reagents.

Results and Discussion

The required sulfide, 2-[2-(benzylthio)benzoyl]pyrrole (**1**), was prepared in 83% yield by reacting pyrrole with methylmagnesium chloride followed by the addition of ethyl 2-(benzylthio)benzoate to this mixture.[13] When **1** was treated with NBS (5 equiv) in chloroform at room temperature for 18 h, the tribrominated heterocyclic compound **2** was formed in 19% yield. Use of lesser amounts of NBS gave inseparable mixtures in which mono- and dibrominated analogues of **2** as well as **2** and unreacted starting material were present in varying amounts, as evidenced by mass spectral analysis of the crude product.



1 2

The reaction of **1** with NCS (5 equiv) in $CHCl_3$ produced **3** as a minor product. The major product exhibited a substantially lower R_f on TLC and exhibited intense blue fluorescence under UV light. The ^{1}H NMR revealed a pair of complex multiplets which appeared to be due to an ethyl group adjacent to a chiral center. The

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(1) (a) Bates, *D.* K.; Tafel, *K.* A.; Xu, J. *Heterocycl. Commun.* **1996**, *2*, 115. (b) Bates, *D.* K.; Habib, *Q.* A. *J. Heterocycl. Chem.* **1995**, *32*, 1477. (c) Bates, *D.* K.; Tafel, *K.* A. *J. Org. Chem.* **1994**, *59*, 8076.

(2) (a) Picard, *J.* A.; Chen, S.; Bates, *D.* K. *Heterocycles* **1994**, *38*, 1775. (b) Tafel, *K.* A.; Bates, *D.* K. *J. Org. Chem.* **1992**, *57*, 3676.

(3) Roitman, J. N.; Mahoney, *N.* E.; Janisiewicz, *W.* J. *Appl. Microbiol. Biotechnol.* **1990**, *34*, 381.

(4) (a) Rao, *K.* A.; Reddy, *G.* C. *J. Agric. Food Chem.* **1990**, *38*, 1260. (b) Durham, *D.* G.; Hughes, *C.* G.; Rees, *A.* H. *Can. J. Chem.* **1972**, *50*, 3223.

(5) Laatsch, H.; Renneberg B.; Hanefeld, U.; Kellner, M.; Pudleiner, H.; Hamprecht, G.; Kraemer, H.; Anke, H. *Chem. Pharm. Bull.* **1995**, *43*, 537.

(6) Renneberg, B.; Kellner, M.; Laatsch, H. *Liebigs Ann. Chem.* **1993**, 847.

(7) Zincke, T. *Chem. Ber.* **1911**, *44*, 769.

(8) Kharasch, N.; Langford, *R.* B. *J. Org. Chem.* **1963**, *28*, 1903.

(9) Bekker, *R.* A.; Popkova, *V.* Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 1123.

(10) Buchanan, *D.* N. *Diss. Abstr. Int. B* **1970**, *31*, 3254.

(11) Skatteboel, L.; Boulette, B.; Solomon, S. *J. Org. Chem.* **1967**, *32*, 3111.

(12) (a) Muchowski, *J.* M.; Galeazzi, E.; Greenhouse, R.; Guzman, A.; Perez, V.; Ackerman, N.; Ballaron, *S.* A.; Rovito, *J.* R.; Tomolonis, *A.* J.; Young, *J.* M.; Rooks, *W.* H. *J. Med. Chem.* **1989**, *32*, 1202. (b) Franco, F.; Greenhouse, R.; Muchowski, *J.* M. *J. Org. Chem.* **1982**, *47*, 1682.

(13) Nicolaou, *K.* C.; Claremon, *D.* A.; Papahatjis, *D.* P. *Tetrahedron Lett.* **1981**, *22*, 4647.

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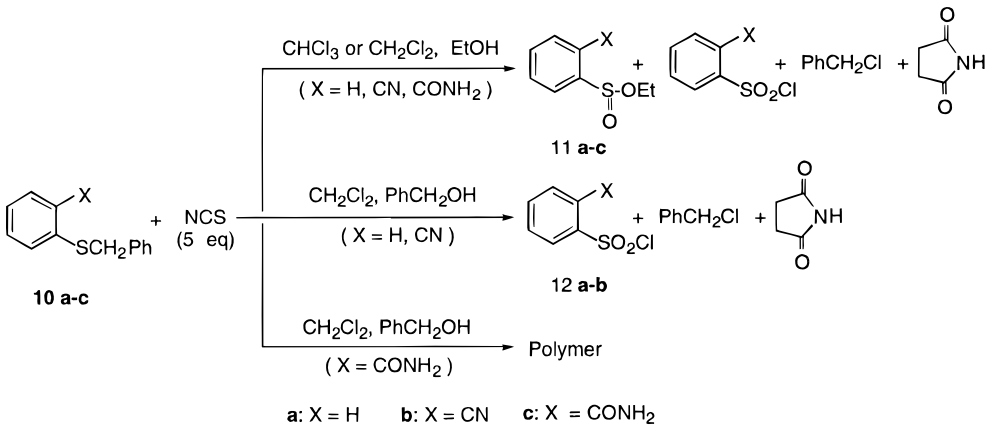
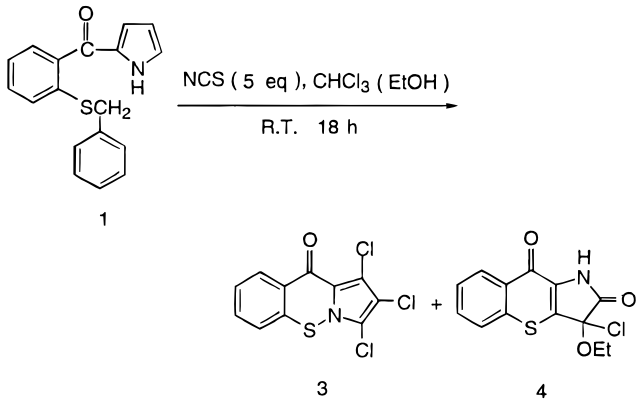
Scheme 1

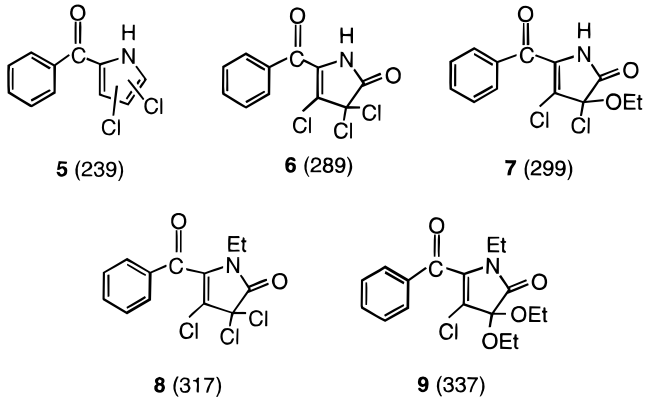


chemical shift of this complex methylene group signal was around 3.5 ppm suggesting an ethoxyl group. Structure **4** is assigned to this product based upon spectral data and elemental analysis.



The ethoxyl group apparently arises from ethanol (~1.1%) which is used to stabilize commerical $CHCl_3$. If additional ethanol (7 equiv) is added to the reaction mixture prior to addition of NCS, very little **3** is formed and **4** may be isolated in 45% yield. If the reaction is conducted in ethanol-free chloroform, inseparable mixtures of the dichlorinated analogue of **3** as well as **3** and other unidentified materials are present.[14] This lack of selectivity of pyrrole ring halogenation is reminiscent of the free radical chlorination of 2-pyrrolecarboxylate esters with *tert*-butyl hypochlorite.[15] Five equivalents of NCS is an optimal choice for the formation of **4**. Addition of more NCS does not improve the yield of **4**. Use of less than 5 equiv of NCS gave mixtures of various halogenated products and a little **4**.

To more fully understand the nature of the reaction forming **4**, we investigated simpler compounds, *i.e.*, 2-benzoylpyrrole which contains no sulfur and other benzyl aryl sulfides which contain no pyrrole ring. Treatment of 2-benzoylpyrrole with NCS (5 equiv) gave a complex mixture of products. Mass spectral analysis of the mixture indicates the presence of compounds with molecular weights of 239, 289, 299, 317, and 337, suggesting the presence of compounds **5**−**9**.

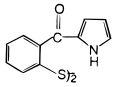


Compounds **8** and **9** undoubtedly arise via *N*-alkylation of intermediates by ethyl chloride which is formed during the reaction. Due to the complexity of the mixture, we did not pursue this reaction further. This reaction of NCS with 2-benzoylpyrrole is significantly more complex and less controllable than other procedures reported for halogenation of 2-aroylpyrroles and alkyl 2-pyrrolecarboxylates.[16] We also briefly investigated the reaction of the parent cyclized ring system, pyrrolo[1,2-*b*][1,2]-benzothiazin-10-one (the nonhalogenated counterpart to **3**), with NCS in $CHCl_3$/EtOH, assuming this compound might be an intermediate in the pathway to **4**. It is not. No **4** is produced in this reaction although several as yet unidentified compounds are formed. Neither **2** nor **3** reacts with ethanol on prolonged exposure. Compound **3** is recovered unchanged after treatment with NCS (1 equiv) in ethanol at rt.

Reactions of "simple" benzyl aryl sulfides **10** with excess NCS/$CHCl_3$ or CH_2Cl_2 did not produce α-chloro sulfides in the presence of an added alcohol. Sulfinic esters and/or sulfonyl chlorides were the major products, depending on the sulfide and the alcohol. The results are summarized in Scheme 1.

When benzyl aryl sulfides **10a**−**c** were treated with 5 equiv of NCS in the presence of added ethanol, the ethyl arenesulfinic esters **11a**−**c** were produced in 30%, 97%, and 42% yields, respectively, along with benzyl chloride,

(14) 1,2,3-Trichloropyrrolo[1,2-*b*][1,2]benzothiazin-10-one is also formed by the reaction of 2-[2-(benzylthio)benzoyl]pyrrole or the corresponding disulfide **i** with excess thionyl chloride in refluxing *p*-xylene in 18% and 24% yields, respectively.

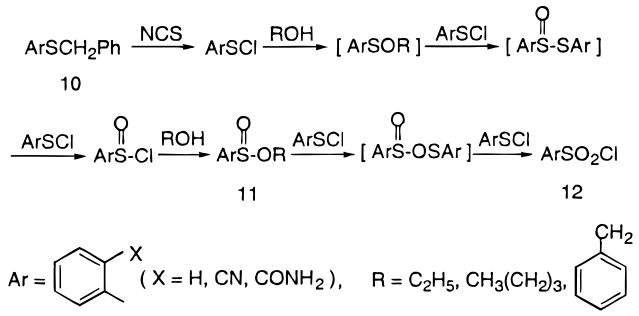


i

(15) Hodges, P.; Richards, *R.* W. *J. Chem. Soc.* **1965**, 459.

(16) (a) Anderson, *H.* J.; Lee, *S.* F. *Can. J. Chem*, **1965**, *43*, 409. (b) Petruso, S.; Caronna, S. *J. Heterocycl. Chem.* **1992**, *29*, 355. (c) Renneberg, B.; Kellner, M.; Laatsch, H. *Ann. Chem.* **1993**, 847.

Scheme 2



succinimide, and small amounts of arenesulfonyl chloride. Similar results were obtained in the presence of added 1-butanol. *This is a previously unreported reaction of benzyl sulfides with NCS and is a simple, convenient source of alkyl arenesulfinates.*[17,18]

The reaction works well with simple *n*-alkyl alcohols, but alcohols having a good leaving group (*i.e.*, benzyl alcohol) work poorly. This is related to the proposed mechanism and is discussed below. Added benzyl alcohol (7 equiv) produces either solely or predominantly an arenesulfonyl chloride. With **10c** an intractable polymer is formed, perhaps due to linear condensation polymerization of sulfonyl chloride with amide NH_2. These data are consistent with a mechanism in which the benzylic C−S bond is broken, forming an intermediate sulfenyl chloride. Douglass and Koop[19,20] reported that methanesulfenyl chloride and methanol form methyl chloride, methanesulfinyl chloride, methyl methanesulfinate, and methanesulfonyl chloride. Their mechanistic rationale, applied to benzyl aryl sulfides, is as shown in Scheme 2.

Support for this mechanism is provided by the reaction products in the presence of benzyl alcohol. In this case, arenesulfinate ester **11** bears a good leaving group (R = benzyl). One would predict a more facile conversion of **11** to sulfonyl chloride **12** than in other cases where R = *n*-alkyl, as observed experimentally. Rather than NCS providing a chlorine source to form the arenesulfenyl chloride and benzyl chloride, it is also possible that NCS reacts with the sulfide directly[12] forming benzyl chloride and an arylsulfenamide. *N*-Arylthioimides are well-known sulfenylation reagents.[21]

It should be noted that in this process some of the ArSCl originally formed becomes $(ArS)_2$. We did not observe significant diaryl disulfide in these reactions, apparently due to its conversion back to ArSCl by excess NCS present in the reaction.

Conclusion

1,2,3-Trihalopyrrolo[1,2-*b*][1,2]benzothiazin-10-ones are produced from 2-[2-(benzylthio)benzoyl]pyrrole (**1**) and excess (5 equiv) NBS or NCS in $CHCl_3$. However if ethanol is present in the NCS reaction, compound **4** is formed. The related compound 1,2,3-trichloropyrrolo[1,2-*b*][1,2]benzothiazin-10-one is also formed by the reaction of compound **1** or the corresponding disulfide with excess $SOCl_2$.

A novel route to alkyl arenesulfinic esters has also been discovered. Treatment of a benzyl aryl sulfide with excess (5 equiv) NCS in the presence of a simple *n*-alkyl alcohol (7 equiv) produces an *n*-alkyl arenesulfinic ester in good yield. An arenesulfonyl chloride is the major product in the presence of benzyl alcohol.

Experimental Section

All reagents were used without purification unless otherwise noted. Silica gel (70−230 mesh, 60 Å) was used for column chromatography. Analytical TLC was performed on silica plates containing a fluorescent indicator developed with chloroform. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, in $CDCl_3$ solution, unless otherwise noted. Mass spectra were recorded at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

2-[2-(Benzylthio)benzoyl]pyrrole (1). Commercial methylmagnesium chloride in THF (25 *mL*, 0.075 mol) was added to toluene (100 *mL*) at 0 °C. To this cold mixture pyrrole was added (5.0 g, 0.075 mol) dropwise under N_2. The solution was heated at 60 °C for 30 min and allowed to cool to rt; then a solution of ethyl 2-(benzylthio)benzoate (9.0 g, 0.033 mol) in toluene (15 *mL*) was added dropwise under N_2. The resulting mixture was refluxed for 22 h and cooled to rt, the reaction was quenched by the addition of saturated NH_4Cl solution, and finally the mixture was acidified to pH 3 with 10% aqueous HCl solution. Following removal of the organic layer, the aqueous layer was extracted with $CHCl_3$ (2 × 80 *mL*), and the combined organics were washed with water (2 × 80 *mL*) and dried (Na_2SO_4). After the solvent was removed *in vacuo*, the resulting crude product was chromatographed (SiO_2, $CHCl_3$) to yield 8.0 g (83%) of **1** as yellow-brown crystals (mp 108−110 °C): ^1H NMR (200 MHz, $CDCl_3$) δ 9.78 (br s, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.38 (m, 2H), 7.25 (m, 6H), 7.12 (m, 1H), 6.57 (m, 1H), 6.27 (m, 1H), 4.10 (s, 2H); IR (KBr) 3279, 1607, 1398 cm^{-1}; MS [*m*/*z* (rel intensity)] 293 (M^+, 1.4), 202 (100.0), 91 (79.0). Anal. Calcd for $C_{18}H_{15}NOS$: C, 73.69; H, 5.15; N, 4.77. Found: C, 73.61; H, 5.35; N, 4.70.

1,2,3-Tribromopyrrolo[1,2-*b*][1,2]benzothiazin-10-one (2). A solution of **1** (0.5 g, 1.7 mmol) and *N*-bromosuccinimide (1.5 g, 8.5 mmol) in $CHCl_3$ (20 *mL*) was stirred at rt for 18 h. The reaction mixture was worked up with $CHCl_3$ (50 *mL*), and H_2O (2 × 25 *mL*) and dried (Na_2SO_4). After solvent removal *in vacuo*, the resulting dark residue was chromatographed (SiO_2, $CHCl_3$) to afford 0.14 g (19%) of **2** as yellow crystals (mp 245−247 °C): ^1H NMR (200 MHz, $CDCl_3$) δ 8.48 (dd, J = 1.6, 8.2 Hz, 1H), 7.63 (m, 1H), 7.50 (m, 2H); IR (KBr) 1703, 1320, 1282 cm^{-1}; UV (methanol) 252 nm (log ϵ = 4.50); MS [*m*/*z* (rel intensity)] 441 (M + 6, 20.7), 439 (M + 4, 58.5), 437 (M + 2, 58.4), 435 (M^+, 20.9), 358 (100.0), 330 (40.8); Anal. Calcd for $C_{11}H_4Br_3NOS$: C, 30.17; H, 0.92; N, 3.20. Found: C, 30.12; H, 0.93; N, 3.15.

1,2,3-Trichloropyrrolo[1,2-*b*][1,2]benzothiazin-10-one (3). Method I. A stirred solution of **1** (1.0 g, 3.4 mmol) and thionyl chloride (8.0 *mL*, 0.11 mol) in *p*-xylene (35 *mL*) was refluxed for 18 h. After cooling to rt, all the volatiles were removed *in vacuo*, and the residue was dissolved in $CHCl_3$ (50 *mL*), washed with H_2O (2 × 20 *mL*), and dried (Na_2SO_4). After the solvent was removed, the dark residue was chromatographed (SiO_2, CH_2Cl_2) to afford 0.19 g (18%) of product **3** as yellow crystals (mp 208−210 °C): ^1H NMR (200 MHz, $CDCl_3$) δ 8.48 (dd, J = 1.4, 8.5 Hz, 1H), 7.64 (m, 1H), 7.46 (m, 2H); IR (KBr) 1700, 1328, 1293 cm^{-1}; UV (methanol) 250 nm (log ϵ = 4.38); MS [*m*/*z* (rel intensity)] 307 (M + 4, 17.0), 305 (M + 2, 47.9), 303 (M^+, 47.9), 267 (100.0), 240 (28.7). Anal. Calcd for $C_{11}H_4Cl_3NOS$: C, 43.28; H, 1.32; N, 4.60. Found: C, 43.28; H, 1.48; N, 4.24.

Method II. A mixture of 2-(2,2′-dithiobenzoyl)pyrrole (disulfide **i**; 0.22 g, 0.55 mmol) and thionyl chloride (40 *mL*, 0.55 mol) treated as in method I gave 0.08 g (24%) of **3**.

(17) Whitesell, J. K.; Wong, M. J. *Org. Chem.* **1994**, *59*, 597.
(18) For a review of sulfinic acids and their derivatives, see: Sterling, C. J. M. *Int. J. Sulfur Chem. B*, **1971**, *6*, 277. Drabowicz, J.; Kielbasinski, P.; Mikolajczyk, M. In *Chemistry of Sulfenic Acids and Their Derivatives*; Patai, S., Ed.; Wiley: Chichester, U.K., 1990.
(19) Douglass, I. B. *J. Org. Chem.* **1974**, *39*, 563.
(20) Douglass, I. B.; Koop, D. A. *J. Org. Chem.* **1962**, *27*, 1398.
(21) (a) Woulfe, S. R.; Iwagami, H.; Miller, M. J. *Tetrahedron Lett.* **1985**, *26*, 3891 and references therein. (b) Gilow, H. M.; Brown, C. S.; Copeland, J. N.; Kelly, K. E. *J. Heterocycl. Chem.* **1991**, *28*, 1025.

Representative Procedure for the Reaction of Benzyl Aryl Sulfides with Excess NCS. NCS (5 equiv) was added portionwise to a well-stirred solution of the appropriate benzyl aryl sulfide (1 equiv) in $CHCl_3$ or CH_2Cl_2 (appropriate volume to afford [sulfide] = 0.1 M) and alcohol (7 equiv) at rt. The mixture was stirred for 18 h. After most of the succinimide was removed by filtration, solvent was removed from the filtrate and the residue was chromatographed (SiO_2, $CHCl_3$).

Compound 4. 0.2 g (45%) obtained from 0.44 g of **1** (in $CHCl_3$/EtOH); yellow solid which exhibited intense blue fluorescence under UV light; 185−188 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 1.7, 7.8 Hz, 1H), 7.54 (td, J = 1.7, 7.8 Hz, 1H), 7.31 (m, 2H), 6.66 (br s, 1H), 3.58 (m, 1H), 3.48 (m, 1H), 1.14 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 164.9, 142.9, 135.6, 134.9, 130.6, 127.04, 126.99, 126.4, 125.3, 85.8, 60.0, 15.0; IR (KBr) 3242, 1738, 1703, 1197 cm^{-1}; MS [*m*/*z* (rel intensity)] 295 (M^+, 3.4), 260 (62.1), 232 (100.0), 214 (61.4). Anal. Calcd for $C_{13}H_{10}ClNO_3S$: C, 52.79; H, 3.41; N, 4.74. Found: C, 52.61; H, 3.45; N, 4.76.

Compound **4** is formed in $CHCl_3$ solution even when no ethanol is added. Commercial $CHCl_3$ is typically stabilized by addition of ethanol (1.1%), which provides **3** and **4**, though in a different ratio.

Ethyl benzenesulfinate (11a):[22] 0.51 g (30%) obtained from 2.0 g of **10a** (in CH_2Cl_2/EtOH); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.53 (m, 3H), 4.09 (m, 1H), 3.71 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.7, 133.8, 133.2, 132.2, 64.9, 15.4; IR (KBr) 1188, 1143 cm^{-1}; MS [*m*/*z* (rel intensity)] 170 (M^+, 24.8), 142 (42.0), 125 (48.7), 51 (100.0).

***n*-Butyl benzenesulfinate:**[22] 0.69 g (35%) obtained from 2.0 g of **10a** (in CH_2Cl_2/1-butanol); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67 (m, 2H), 7.50 (m, 3H), 4.04 (m, 1H), 3.59 (m, 1H), 1.55 (m, 2H), 1.31 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.9, 133.0, 130.0, 126.2, 65.6, 32.7, 20.0, 14.5; IR (KBr) 1199, 1135 cm^{-1}; MS [*m*/*z* (rel intensity)] 198 (M^+, 2.6), 143 (100.0), 125 (47.9), 57 (67.5).

Ethyl 2-cyanobenzenesulfinate (11b): 1.1 g (97%) prepared from 1.3 g of **10b** (in $CHCl_3$/EtOH); pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97 (m, 1H), 7.62−7.77 (m, 3H), 4.26 (m, 1H), 4.02 (m, 1H), 1.31 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 147.8, 133.8, 133.2, 132.2, 125.3, 115.0, 110.2, 64.9, 15.5; IR (KBr) 2229, 1384, 1138 cm^{-1}; MS [*m*/*z* (rel intensity)] 195 (M^+, 2.1), 167 (7.9), 150 (11.3), 103 (100.0).

2-(Ethoxysulfinyl)benzamide (11c): 0.54 g (42%) obtained from 1.45 g of **10c** (in $CHCl_3$/EtOH); white solid; mp 78−80 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02 (m, 1H), 7.79 (m, 1H), 7.57 (m, 2H), 5.90 (br s, 2H), 4.37 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.8, 141.7, 132.6, 132.1, 130.9, 130.6, 128.5, 62.9, 14.3; IR (KBr) 3311, 1722, 1440, 1140 cm^{-1}; MS [*m*/*z* (rel intensity)] 213 (M^+, 94.0), 185 (67.0), 184 (100.0). Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57. Found: C, 50.38; H, 5.11; N, 6.46.

Benzenesulfonyl chloride (12a): 1.1 g (62%) obtained from 2.0 g of **10a** (in CH_2Cl_2/$PhCH_2OH$); identified by comparison with an authentic sample.

2-Cyanobenzenesulfonyl chloride (12b):[23] 0.71 g (59%) obtained from 1.35 g of **10b** (in CH_2Cl_2/$PhCH_2OH$); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.19 (m, 1H), 7.95 (m, 1H), 7.87 (m, 2H); IR (KBr) 2235, 1385, 1190 cm^{-1}; MS [*m*/*z* (rel intensity)] 201 (M^+, 4.8), 166 (46.5), 102 (100.0).

Supporting Information Available: Copies of ^{13}C NMR spectra of **4**, **11a**−**c**, and *n*-butyl benzenesulfinate (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead for ordering information.

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(22) Takata, T.; Kim, *Y.* H.; Oae, S. *Tetrahedron Lett.* **1978**, *44*, 4303.

(23) Yoon, *Y.* J.; Kang, *Y.* S. *Bull. Korean Chem. Soc.* **1985**, *6*, 51.