Directed ortho Metalation of O-Aryl and O-Pyridyl Thiocarbamates. A Versatile Synthetic Method for Substituted Phenol into Thiophenol Conversion

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The preparation of ortho-substituted O-aryl and O-pyrid-3-yl thiocarbamates 7a–h and 11a–d and anionic ortho-Fries rearrangements of selected cases, [O-phenyl N,N-diethyliothiocarbamate (6a) → N,N-diethyl-2-hydroxy-3-methylbenzenearboxothioamide (9), O-[4-(trimethylsilyl)pyridyl-3-yl] N,N-diethyliothiocarbamate (11a) → N,N-diethyl-3-hydroxy-4-(trimethylsilyl)pyridine-3-carboxothioamide (13)], via the directed ortho metalation protocol are described; coupled with their further thermal conversion (Kwart–Newman rearrangement) into S-thiocarbamates 8a–f and 12a–b and simple hydrolysis, this constitutes a new methodology for phenol to ortho-substituted thiophenol conversion (4 → 5).

Among the large number of oxygen-based directed metalation groups (DMGs) which productively participate in the directed ortho-metalation protocol, 1 (Scheme 1) the original OMe, 2a and the versatile OMOM 2b and OCONET 2c presently enjoy the most synthetic utility while the OTHP 2d and the OMEM 2e and OP(O)(NR2)2 2f and OSEM 2g constitute old underdeveloped and new inadequately tested DMGs respectively. This fundamental reaction, when followed by moderately acidic, basic, or fluoride (OSEM) deprotection procedures, 2 → 1, is a flexible and convenient route for regiospecific access to a variety of ortho-substituted phenols. The OCONET 2 DMG embodies an added synthetic advantage in that it serves as a “carrier” for the CONET 1 DMG, transferring it by an anionic ortho-Fries rearrangement, 2 2 → 3, into a position poised (after OH protection) for further metalation chemistry. Herein we report on the ortho metalation of O-aryl and O-pyridyl thiocarbamates 6 and 10, which not only provides a new route to products 7 and 11 respectively but also, by virtue of the Kwart–Newman rearrangement, 2 leads to the corresponding S-thiocarbamates thus demonstrating, with understood hydrolysis, the overall phenol to ortho-substituted thiophenol conversion, 4 → 5. 3

![Scheme 1]

Exploratory studies with readily available (see Experimental) O-phenyl N,N-diethyliothiocarbamate (6a) led to standardization of optimum conditions (2.2 equiv s-BuLi/TMEDA/THF, -78 °C, 1 h) for generation of ortho-lithiated species which then was quenched with electrophiles to give a variety of substituted products 6b and 7a–h generally in good yields (Table 1). The reaction with benzonitrile gave a thiocarbamoyl O to O migration product 7f, analogous to the result observed in part with the corresponding carbamate. 6 However, the normal condensation product 7f was obtained by quenching the reaction mixture with aqueous ammonium chloride at -78 °C (see Experimental). Contrary to the o-tolyl carbamate which showed nonselective C-6 and ortho-methyl deprotonation, 6 the corresponding thiocarbamate 6b, under the same conditions, smoothly afforded
C-6 substituted products 7g and 7h. Regiospecific 2-substitution of O-naphth-1-yl thio carbamate (6c) was also cleanly achieved. Lithium 2,2,6,6-tetramethylpiperidide deprotonation of O-aryl-3-yl thio carbamate 10 followed by electrophile quench afforded products 11a–d (Table 2), the required base and site of metalation being in consonance with results observed for the corresponding carbamate. The corresponding O-pyrid-2-yl thio carbamate showed poor regioselectivity in anion formation under these and other conditions affording a mixture of 3- and 6-substituted and 3,6-disubstituted products after chlorotrimethylsilane quench, while metalation of the O-pyrid-4-yl thio carbamate was unsuccessful under these conditions.

The anionic ortho-Fries rearrangement was performed on O-aryl 6b and O-pyridyl 11a thio carbamates to provide the thioamides 9 and 13, respectively, in good yields.

According to the originally recommended conditions (Ph3O, reflux),4 O-aryl 7 and O-pyridyl 11 thio carbamates underwent smooth Kwart–Newman rearrangement to furnish the S-thio carbamates 8a–f and 12a–b respectively in excellent yields. To demonstrate overall phenol to ortho-substituted thiophenol conversion, compounds 8d and 12b were hydrolyzed to respective ortho-substituted thiophenol and pyridimethiol derivatives which were isolated as the corresponding disulfides (see Experimental).

Based on these studies, the wider use of this directed metalation-mediated phenol to thiophenol strategy, 4 → 5, for the construction of polysubstituted aromatics and heteroaromatics may be anticipated.
Melting points were determined on a Buchi SMP-20 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. 'H NMR spectra and 13C NMR spectra were recorded on Bruker AC-200 or AM-250 instruments in CDCl3 solution. Mass spectra (MS) were determined on a high-resolution Varian MAT-CH7 spectrometer.

BuLi, s-BuLi, i-Pr2NH, 2,2,6,6-tetramethylpiperidide and N,N,N',N'-tetramethylthelyenediamine (TMEDA) were purchased from Aldrich Chemical Co. i-Pr2NH, 2,2,6,6-tetramethylpiperidide and TMEDA were dried and distilled from CaH2 and stored under argon. The titr of all alkylithium reagents were determined with 2,5-hexanediol diethyl ether as standard. 2 THF and Et2O were freshly distilled from sodium benzenophene ketyl prior to use. Metallation reactions were performed in oven- or flame-dried glassware under argon, using syringe-septum cap techniques. The phrase normal workup is the equivalent of addition of water or sat. NH4Cl solution, extraction with Et2O, washing the organic extract with sat. brine solution, drying (Na2SO4), filtration, and evaporation to dryness in vacuo. TLC was performed on E-Merck silica gel 60 strips and medium pressure column chromatography was carried out on BDH silica gel 60 (0.04–0.063 mm and 0.063–0.20 mm).

**O-Pheny N,N-Diethylthiocarbamate (6a): Typical Procedure:**

Following a literature method,44 a solution of phenol (0.500 g, 5.32 mmol) in DMF (20 mL) was added to a suspension of NaH (0.140 g, 5.85 mmol) in DMF (20 mL) and stirred at 0 °C. After hydrolysis, the reaction mixture was added to a solution of N,N-diethylthiocarbamoyl chloride2 (1.051 g, 6.92 mmol) in the presence of water (2 × 10 mL), NaOH (0.02 mol), and KOH (0.02 mol), and stirred at 50 °C. The reaction mixture was filtered through a column of silica gel, washed with ethyl acetate (20 mL), and the filtrate was evaporated under reduced pressure. The resulting residue was recrystallized from ethanol to give 6a; yield: 0.28 g (55%); mp: 65–67 °C; Found: C, 45.5; H, 7.0; N, 22.2%. The 1H NMR spectrum of 6a showed a singlet at 6.16 ppm, corresponding to the thioether group. The 13C NMR spectrum showed a peak at 94.2 ppm, corresponding to the carbon of the thioether group. The IR spectrum showed a strong absorption band at 3100 cm⁻¹, corresponding to the carbonyl group of the ester.

**O-Pyrid-3-yl N,N-Diethylthiocarbamate (10):**

A mixture of 6a (0.20 g, 1.00 mmol), s-BuLi (1.93 mL, 2.00 mmol of a 1.14 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with DME (0.23 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/EtOAc 9:1) gave 7a; yield: 0.072 g (50%); yellow oil.

**O-(2-Formylphenyl) N,N-Diethylthiocarbamate (7a):**

A mixture of 6a (0.20 g, 1.00 mmol), s-BuLi (1.93 mL, 2.00 mmol of a 1.14 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with DME (0.23 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/EtOAc 9:1) gave 7a; yield: 0.072 g (50%); yellow oil.

**O-(2-N,N-Diethylthiocarbamoylphenyl) N,N-Diethylthiocarbamate (7b):**

A mixture of 6a (0.20 g, 1.00 mmol), s-BuLi (1.58 mL, 2.20 mmol of a 1.14 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with CICN (0.38 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/EtOAc 6:4) gave 7b; yield: 0.258 g (84%); colorless oil.

**O-Naphth-1-yl N,N-Diethylthiocarbamate (6c):**

The above procedure was adapted using the following quantities of reagents: naphthol (0.993 g, 6.89 mmol), NaH (0.182 g, 7.58 mmol), N,N-diethylthiocarbamoyl chloride (1.257 g, 8.27 mmol); yield: 1.172 g (65%); mp: 96–97 °C (EtOH). HRMS (C13H17N3O2S): calcd. 259.1032; found 259.1028.

**O-o-Tolyl N,N-Diethylthiocarbamate (6b): Typical Procedure for the Metallation of O-Aryl Thiocarbamates:**

To a solution of s-BuLi (1.58 mL, 2.20 mmol of a 1.39 M solution), and TMEDA (0.34 mL, 2.20 mmol) in anhydrous THF (10 mL) at –78 °C, a solution of 0.02 mol of 6a (0.10 g, 2.00 mmol) was added. After stirring at –78 °C for 1 h, the reaction mixture was warmed to room temperature and stirred for 20 min. The resulting mixture was filtered through a column of silica gel, washed with ethyl acetate (20 mL), and the filtrate was evaporated under reduced pressure. The resulting residue was recrystallized from ethanol to give 6b; yield: 0.20 g (88%); colorless oil.

**O-Formylphenyl N,N-Diethylthiocarbamate (7a):**

A mixture of 6a (0.20 g, 1.00 mmol), s-BuLi (1.93 mL, 2.00 mmol of a 1.14 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with DME (0.23 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/EtOAc 9:1) gave 7a; yield: 0.072 g (50%); yellow oil.

**O-(2-N,N-Diethylthiocarbamoylphenyl) N,N-Diethylthiocarbamate (7b):**

A mixture of 6a (0.20 g, 1.00 mmol), s-BuLi (1.58 mL, 2.20 mmol of a 1.14 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with CICN (0.38 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/EtOAc 6:4) gave 7b; yield: 0.258 g (84%); colorless oil.

**H NMR (CDCl3): δ (rel intensity) = 11.3 (19), 13.1 (20), 44.0 (18), 48.1 (16), 123.1 (14), 130.1 (14), 144.2 (19), 146.2 (16), 150.0 (6), 185.6 (4).**

**O-Naphth-1-yl N,N-Diethylthiocarbamate (6c):**

The above procedure was adapted using the following quantities of reagents: naphthol (0.993 g, 6.89 mmol), NaH (0.182 g, 7.58 mmol), N,N-diethylthiocarbamoyl chloride (1.257 g, 8.27 mmol); yield: 1.172 g (65%); mp: 96–97 °C (EtOH). HRMS (C13H17N3O2S): calcd. 259.1032; found 259.1028.

**MS (70 ev): m/z (%) = 259 (M⁺, 33), 116 (60), 100 (100), 88 (72), 32.**

**IR (KBr): ν = 1220, 1516 cm⁻1.**

**1H NMR (CDCl3): δ (rel intensity) = 1.38, 1.44 (21, 3 H each, J = 7.1 Hz), 3.84, 3.96 (2 q, 2 H each, J = 7.1 Hz), 7.21 (m, 11 H), 7.47 (m, 37 H), 7.83 (m, 37 H).**

**13C NMR (CDCl3): δ (rel intensity) = 11.7 (18), 13.5 (14), 44.2 (12), 48.2 (12), 113.9 (18), 121.4 (13), 125.1 (17), 125.8 (13), 126.1 (13), 126.2 (14), 127.5 (3), 127.9 (16), 134.4 (3), 149.7 (2), 186.7 (2).**

**O-Formylphenyl N,N-Diethylthiocarbamate (7a):**

A mixture of 6a (0.20 g, 1.00 mmol), s-BuLi (1.93 mL, 2.00 mmol of a 1.14 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with DME (0.23 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/EtOAc 9:1) gave 7a; yield: 0.072 g (50%); yellow oil.

**O-(2-N-N-Diethylthiocarbamoylphenyl) N,N-Diethylthiocarbamate (7b):**

A mixture of 6a (0.20 g, 1.00 mmol), s-BuLi (1.58 mL, 2.20 mmol of a 1.14 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with CICN (0.38 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/EtOAc 6:4) gave 7b; yield: 0.258 g (84%); colorless oil.
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MS (70 eV): m/z (%) = 308 (M+, 9), 116 (25), 100 (100), 88 (13), 72 (61).
IR ( neat): ν = 1210, 1513, 1631 cm⁻¹.
¹H NMR (CDCl₃): δ = 1.20 (m, 12 H), 3.38 (m, 4 H), 3.68 (m, 2 H), 3.82 (m, 2 H), 7.30 (m, 4 H).
¹³C NMR (CDCl₃): δ (rel intensity) = 11.3 (19), 12.0 (21), 13.0 (22), 13.6 (20), 38.2 (16), 43.0 (16), 44.1 (17), 47.7 (16), 124.3 (19), 125.1 (23), 126.1 (19), 129.0 (18), 130.8 (7), 159.7 (4), 166.8 (5), 185.2 (4).

O-(Phenylthio)phenyl N,N-Diethyliothiocarbamate (7c):
A mixture of 6a (0.250 g, 1.10 mmol), s-BuLi (1.74 mL, 2.42 mmol of a 1.39 M solution), and TMEDA (0.36 mL, 2.42 mmol), was treated with PhCHO (0.32 g, 3.30 mmol). Normal workup followed by chromatography (hexane/ EtOAc: 9:1) gave 7c; yield: 0.295 g (85%); colorless oil.
HRMS (C₂₇H₂₄NO₂S): calc. 317.0910; found 317.0891.
MS (70 eV): m/z (%) = 317 (M⁺, 5), 208 (100), 116 (87), 100 (97), 88 (70), 72 (36), 60 (45).
IR ( neat): ν = 1204, 1513 cm⁻¹.
¹H NMR (CDCl₃): δ = 1.25, 1.32 (2 t, 3 H each, J = 7.1 Hz), 3.60, 3.89 (2 q, 2 H each, J = 7.1 Hz), 7.25 (m, 9 H).
¹³C NMR (CDCl₃): δ (rel intensity) = 11.5 (7), 13.2 (7), 44.0 (8), 48.1 (7), 124.0 (7), 126.4 (7), 126.9 (7), 127.8 (8), 128.9 (18), 128.9 (2), 130.9 (16), 132.5 (9), 134.7 (12), 152.3 (2), 185.6 (1).

O-[2-Hydroxyphenyl][benzyl] N,N-Diethyliothiocarbamate (7f):
A mixture of 6a (0.209 g, 1.00 mmol), s-BuLi (1.58 mL, 2.22 mmol of a 1.39 M solution), and TMEDA (0.34 mL, 2.20 mmol), was treated with PhCHO (0.31 mL, 3.00 mmol). Normal workup followed by chromatography (hexane/ EtOAc: 8:2) gave 7f; yield: 0.252 g (80%); mp 127–128°C (EtO).
HRMS (C₂₇H₂₄NO₂S): calc. 315.1282; found 315.1282.
MS (70 eV): m/z (%) = 315 (M⁺, 10), 183 (61), 181 (100), 15 (72). 
IR (KrBr): ν = 1134, 1258, 1600, 1632, 3247 cm⁻¹.
¹H NMR (CDCl₃): δ = 1.15, 1.19 (2 t, 3 H each, J = 7.1 Hz), 3.42 (m, 4 H), 6.19 (s, 1 H), 6.77 (dddt, 1H), 1J = 1.3, 7.9 Hz), 6.93 (dd, 1H, J = 1.3, 8.1 Hz), 6.99 (dd, 1H, J = 1.7, 7.9 Hz), 7.11 (dddt, 1H, 1J = 1.7, 8.1 Hz), 7.35 (m, 5 H), 8.37 (br, 1H, D₂O exchangeable).
¹³C NMR (CDCl₃): δ (rel intensity) = 13.0 (2), 13.5 (2), 42.5 (2), 42.7 (2), 46.9 (6), 117.7 (7), 120.4 (9), 127.1 (4), 128.4 (20), 128.5 (18), 129.2 (8), 140.3 (5), 154.1 (3), 168.5 (2).

O-[6-Methyl-2-(trimethylsilyl)phenyl] N,N-Diethyliothiocarbamate (7g):
A mixture of 6b (0.265 g, 1.19 mmol), s-BuLi (2.06 mL, 2.62 mmol of a 1.30 M solution), and TMEDA (0.39 mL, 2.62 mmol), was treated with Me₃SiCl (0.45 mL, 3.57 mmol). Normal workup followed by chromatography (hexane/ EtOAc: 9:1) gave 7g; yield: 0.207 g (59%); yellow oil.
HRMS (C₃₂H₂₄NO₂S): calc. 395.1428; found 395.1412.
MS (70 eV): m/z (%) = 295 (M⁺, 10), 280 (13), 222 (32), 116 (34), 100 (100), 88 (19), 72 (19).
IR ( neat): ν = 1163, 1507 cm⁻¹.
¹H NMR (CDCl₃): δ = 0.27 (s, 9 H), 1.31, 1.35 (2 t, 3 H each, J = 7.1 Hz), 2.18 (s, 3 H), 3.56, 3.78, 4.00, 4.07 (4 q, 1H each, J = 7.1, 13.8 Hz), 7.19 (m, 2H), 7.35 (dd, 1H, J = 2.0, 6.8 Hz).
¹³C NMR (CDCl₃): δ (rel intensity) = 0.34 (14), 11.6 (7), 13.4 (9), 17.0 (7), 43.4 (8), 47.6 (7), 125.7 (8), 130.9 (2), 132.4 (7), 132.8 (7), 157.0 (1), 186.1 (2).

O-[6-Methyl-2-(trimethylstannyl)phenyl] N,N-Diethyliothiocarbamate (7h):
A mixture of 6b (0.446 g, 2.00 mmol), s-BuLi (3.50 mL, 4.40 mmol of a 1.26 M solution), and TMEDA (0.66 mL, 4.40 mmol), was treated with Me₃SnCl (1.20 g, 6.00 mmol). Normal workup followed by chromatography (hexane/ EtOAc: 9.5:0.5) gave 7h; yield: 0.433 g (56%); colorless oil.
MS (70 eV): m/z (%) = 372 (10), 222 (100), 116 (21), 100 (20), 88 (14), 72 (14).
IR ( neat): ν = 1159, 1501 cm⁻¹.
¹H NMR (CDCl₃): δ = 0.28 (s, 9 H), 1.31, 1.35 (2 t, 3 H each, J = 7.1 Hz), 2.18 (s, 3 H), 3.51, 3.73, 3.94, 4.11 (4 q, 1H each, J = 7.1, 14.0 Hz), 7.17 (m, 2H), 7.32 (dd, 1H, J = 2.8, 6.1 Hz).
¹³C NMR (CDCl₃): δ (rel intensity) = 8.6 (26), 11.6 (25), 13.3 (24), 17.1 (12), 43.4 (20), 47.6 (18), 125.9 (19), 130.5 (6), 131.6 (19), 134.0 (20), 135.4 (2), 157.4 (2), 186.1 (3).
**O-[2-(Trimethylsilyl)naphth-1-yl]-N,N-Diethyliiocarbamate (71):** A mixture of O-naphth-1-yl N,N-diethyliiocarbamate (6ε, 0.278 g, 1.07 mmol), s-BuLi (1.80 M, 2.36 mmol of a 1.30 M solution), and TMEDA (0.36 M, 2.36 mmol), was treated with Me2SiCl (0.41 M, 3.22 mmol). Normal workup followed by chromatography (hexane/EtOAc 9:1) gave the product: 71; yield: 0.298 g (84%); yellow oil. HRMS (C28H31NO3S): calc. 331.1428; found 331.1416. MS (70 eV); mz (%) = 331 (M⁺, 6), 316 (45), 116 (86), 100 (100), 88 (48), 72 (31). IR (neat): ν = 1157, 1510 cm⁻¹.

**O-[4-(Trimethylsilyl)pyridin-3-yl]-N,N-Diethyliiocarbamate (11a); Typical Procedure for Metalation of O-Pyridin-3-yl Thio carbamates:** To a solution of LiTMP [prepared by reaction of BuLi (1.13 M, 1.33 mmol of a 1.53 M solution)] and 2,2,6,6-tetramethylpiperidine (0.29 M, 1.73 mmol) in anhyd THF (10 mL) at -78 °C under argon was dropwise added via cannula a solution maintained at 0°C of 10 (0.329 g, 1.57 mmol) in anhyd THF (5 mL). The solution was stirred for 30 min, treated with Me2SiCl (0.40 M, 3.14 mmol), and the mixture was warmed to warm to r.t. over 1-2 h. Normal workup followed by chromatography (hexane/EtOAc 7:3) gave 11a; yield: 0.385 g (87%); colorless oil. HRMS (C25H29NO3S): calc. 282.1224; found 282.1208. MS (70 eV); mz (%) = 282 (M⁺, 12), 116 (37), 100 (100), 88 (24), 72 (22). IR (neat): ν = 1191, 1510 cm⁻¹.

**O-[4-(Phenylthio)pyridin-3-yl]-N,N-Diethyliiocarbamate (11b);** A mixture of 10 (0.410 g, 1.95 mmol), BuLi (1.40 M, 2.15 mmol of a 1.53 M solution), and 2,2,6,6-tetramethylpiperidine (0.36 M, 2.15 mmol), was treated with (PhS)2 (0.640 g, 2.93 mmol). Normal workup followed by chromatography (hexane/EtOAc 7:3) gave 11b; yield: 0.510 g (82%); yellow oil. HRMS (C25H29NO3S): calc. 238.0862; found 238.0844. MS (70 eV); mz (%) = 238 (M⁺, 15), 116 (46), 100 (100), 88 (44), 72 (29). IR (neat): ν = 1215, 1516 cm⁻¹.

**O-[4-(a-Hydroxybenzyl)pyridin-3-yl]-N,N-Diethyliiocarbamate (11c);** A mixture of 10 (0.410 g, 1.95 mmol), BuLi (1.40 M, 2.15 mmol of a 1.53 M solution), and 2,2,6,6-tetramethylpiperidine (0.36 M, 2.15 mmol), was treated with PhCHO (0.30 M, 2.93 mmol). Addition of sat. aq NaH, Cl at -78 °C followed by normal workup and chromatography (hexane/EtOAc 6:4) gave 11c; yield: 0.525 g (85%); mp 101–102 °C (EtOH). HRMS (C30H31NO3S): calc. 316.1247; found 316.1235. MS (70 eV); mz (%) = 316 (M⁺, 12), 210 (22), 209 (20), 184 (27), 116 (30), 100 (100), 88 (32), 84 (95), 72 (37). IR (neat): ν = 1105, 1185, 1521, 2932 cm⁻¹.

**O-[4-(2-Furylhydroxymethyl)pyridin-3-yl]-N,N-Diethyliiocarbamate (11d);** A mixture of 10 (0.210 g, 1.00 mmol), BuLi (0.80 M, 1.20 mmol of a 1.50 M solution), and 2,2,6,6-tetramethylpiperidine (0.20 M, 1.20 mmol), was treated with 2-furfural (0.13 M, 1.50 mmol). Normal workup followed by chromatography (hexane/EtOAc 1:1) gave 11d; yield: 0.280 g (91%); colorless oil. HRMS (C25H18NO4S): calc. 306.1039; found 306.1043. MS (70 eV); mz (%) = 306 (M⁺, 9), 209 (32), 174 (73), 116 (55), 100 (100), 88 (32), 84 (47), 72 (40). IR (neat): ν = 1113, 1218, 1513, 3137 cm⁻¹.

**S-o-Tolyl N,N-Diethyliiocarbamate (8a); Typical Procedure for Rearrangement O-Aryl Thio carbamates into S-Aryl Thio carbamates:** A solution of 6b (0.260 g, 1.17 mmol) in Ph2O (2 mL) was heated at 280–285 °C and the reaction was followed by TLC. Direct chromatography (hexane/EtOAc 9:1) gave 8a; yield: 0.235 g (90%); colorless oil. HRMS (C25H21NO2S): calc. 223.1032; found 223.1025. MS (70 eV); mz (%) = 223 (M⁺, 4), 100 (100), 72 (29). IR (neat): ν = 1248, 1656 cm⁻¹.

**S-[2-Formylphenyl] N,N-Diethyliiocarbamate (8b);** 7a (0.208 g, 1.18 mmol), gave after chromatography (hexane/EtOAc 7:2.5), 8b; yield: 0.185 g (66%); yellow oil. HRMS (C25H19NO3S): calc. 237.0825; found 237.0816. MS (70 eV); mz (%) = 237 (M⁺, 4), 137 (15), 109 (18), 100 (18), 72 (84). IR (neat): ν = 2535, 1660, 1695, 2743, 2869 cm⁻¹.

**S-[2,2'-N,N-Diethyliiocarbamoylphenyl] N,N-Diethyliiocarbamate (8c);** 7b (0.196 g, 0.63 mmol) gave, after chromatography (hexane/EtOAc 1:1), 8c; yield: 0.153 g (78%); colorless oil. HRMS (C31H24NO4S): calc. 308.1560; found 308.1557. MS (70 eV); mz (%) = 308 (M⁺, 32), 208 (32), 199 (14), 100 (99), 72 (100). IR (neat): ν = 1248, 1631, 1659 cm⁻¹.
S-2-(Phenylthio)phenyl \(N\)-(N-Diethylthiocarbamato)(8d): ms (70 eV); \(m/z\) (%) = 317 (M\(^+\)), 208 (25%), 100 (100), 72 (53). IR (neat): \(n_v = 1246, 1663 \text{ cm}^{-1}\). 13\(^C\) NMR (CDCl\(_3\)); \(\delta \text{ (rel intensity) = 12.4 (12), 13.7 (18), 38.3 (12), 42.3 (20), 125.4 (2), 125.7 (12), 128.7 (14), 129.1 (13), 138.0 (15), 142.5 (2), 164.5 (3), 168.9 (3).} \)

**S-(2-Iodosophenyl) N,N-Diethylthiocarbamato (8e):** ms (70 eV); \(m/z\) (%) = 335 (M\(^+\)), 208 (25%), 100 (100), 72 (53). IR (neat): \(n_v = 1247, 1667 \text{ cm}^{-1}\). 13\(^C\) NMR (CDCl\(_3\)); \(\delta \text{ (rel intensity) = 13.1 (1), 42.4 (3), 126.2 (7), 127.7 (5), 128.1 (2), 129.2 (10), 129.4 (5), 129.9 (8), 133.0 (15), 134.0 (2), 137.6 (5), 143.9 (5), 164.2 (2).} \)

**S-(2-Iodomethylphenyl) N,N-Diethylthiocarbamato (8f):** ms (70 eV); \(m/z\) (%) = 282 (M\(^+\)), 247 (47), 267 (22), 194 (42), 178 (72), 70 (100). IR (neat): \(n_v = 1138, 1509, 3152 \text{ cm}^{-1}\). 13\(^C\) NMR (CDCl\(_3\)); \(\delta \text{ (rel intensity) = 1.6 (21), 11.2 (8), 13.7 (8), 47.0 (6), 48.8 (8), 130.2 (14), 138.1 (1), 138.8 (6), 142.0 (1), 155.6 (1), 193.2 (2).} \)

**Bi(2-(phenylthio)phenyl) Disulfide:** Typical Procedure for Hydrolysis of S-Aryl Thiocarbamates into Thiophenols: A solution of 8d (0.220 g, 0.69 mmol) in MeOH/THF (1:1 solution) (10 mL) under nitrogen was slowly treated with KOH pellets (0.155 g, 2.78 mmol). The mixture was refluxed for 5 h, cooled to r.t., and extracted with CH\(_2\)Cl\(_2\) (3 x 10 mL). The organic extract was washed with saturated 5% HCI (30 mL), dried (MgSO\(_4\)), and evaporated to dryness under vacuo. Chromatography (hexane/EtOAc 9:1) gave the product; yield: 0.135 g (90%); mp 124–125°C (EtOH/CH\(_2\)Cl\(_2\)); Lit.\(^{32}\) mp 125–125.5°C.

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(b) Snieckus, V. Chem. Rev. 1990, 90, 879.  
(3) For a comprehensive tabular list of groups which undergo ortho anion-induced 1,3-migration, including the author’s own extensive work in this area, see Hefswinkel, D.; Rudiger, L. *Chem. Ber.* 1985, 118, 66.
For recent applications, see De Lucchi, O.; Fabri, D. *Synlett* 1990, 287.
(5) Recently, the directed ortho metalation of thiophenols to give some ortho-substituted products has been reported: