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SYNTHESIS OF 3-SUBSTITUTED BENZO[*b*]THIOPHENES *VIA* THE REACTION OF α-SUBSTITUTED 2-LITHIO-β-METHOXYSTYRENES WITH SULFUR

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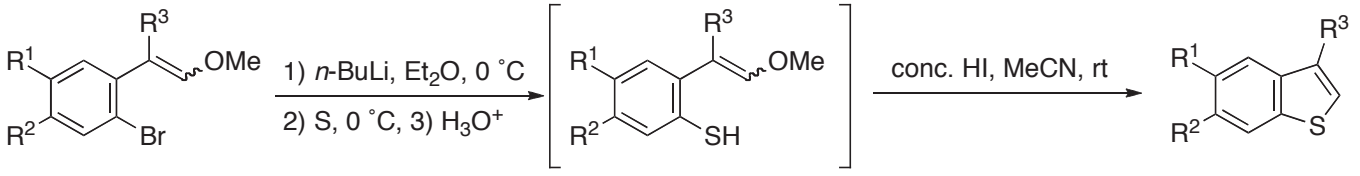
Abstract – 3-Substitued benzo[*b*]thiophenes were synthesized in reasonable overall yields from α-substituted 2-bromo-β-methoxystyrenes. Thus, the bromine-lithium exchange between these bromostyrenes with butyllithium in diethyl ether at 0 ˚C followed by reaction with sulfur afforded the corresponding α-substituted β-methoxy-2-sulfanylstyrenes. These were then treated with an equimolar amount of concentrated hydriodic acid in acetonitrile at room temperature to give the desired products.

The hydriodic acid-catalyzed or -mediated cyclization of β-methoxystyrene derivatives carrying an appropriate functional group at the *o*-position has been successfully employed by us for the synthesis of several benzene-fused heterocyclic compounds.[1] On the other hand, compounds having the benzo[*b*]thiophene skeleton have held considerable interest not only for organic chemists, but also for medicinal chemists, because of their useful biological activities.[2] Accordingly, a number of efficient methods for the preparation of this class of heterocycles have recently been reported.[3] As contribution from our laboratory, we have recently reported four convenient methods starting mainly from 2-sulfanylphenyl ketones and related compounds.[4] We now wish to report a new method for the preparation of 3-substituted benzo[*b*]thiophenes (**3**) starting from α-substituted 2-bromo-β-methoxystyrenes (**1**), which are easily prepared from readily available starting materials according to the previously reported methods.[1,5-7]

Our two-step synthesis of 3-substituted benzo[*b*]thiophenes (**3**) was performed as illustrated in Scheme 1. The α-substituted 2-lithio-β-methoxystyrenes were first generated by the bromine-lithium exchange between **1** and butyllithium in diethyl ether at 0 ˚C. These lithium compounds were allowed to react with sulfur to give, after the usual aqueous workup, the corresponding α-substituted β-methoxy-2-

sulfanylstyrenes (**2**), which were then immediately subjected, without any purification, to treatment with concentrated hydriodic acid. Thus, the solutions of **2** in acetonitrile were bubbled with argon gas to remove oxygen gas, which may cause the oxidation of **2** to the corresponding disulfides, and then were treated with an equimolar amount of concentrated hydriodic acid at room temperature for 1 h. After the usual aqueous workup the resulting crude products were purified by preparative TLC on silica gel to afford the desired products in reasonable overall isolated yields from **1**, as summarized in Scheme 1.



1 **2**

3a $R^1 = R^2 = H$, $R^3 = Me$ 34%
3b $R^1 = R^2 = H$, $R^3 = Ph$ 41%
3c $R^1 = R^2 = H$, $R^3 = 4\text{-}t\text{-}BuC_6H_4$ 44%
3d $R^1 = R^2 = H$, $R^3 = 4\text{-}MeOC_6H_4$ 46%
3e $R^1 = OMe$, $R^2 = H$, $R^3 = 3,4\text{-Xylyl}$ 37%
3f $R^1 = H$, $R^2 = OMe$, $R^3 = m\text{-Tol}$ 45%
3g $R^1 = H$, $R^2 = OMe$, $R^3 = p\text{-Tol}$ 45%

Scheme 1

When the cyclization reactions were carried out using a catalytic amount (0.2–0.5 equiv) of concentrated hydriodic acid under similar reaction conditions, they proceeded sluggishly and did not complete even after extended reaction times. Although the preparation of chlorine substituted 3-arylbenzo[*b*]thiophenes was attempted using α-aryl-2-bromo-β-methoxystyrenes carrying a chloro substituent in either of the benzene nuclei as substrates under the same conditions, only trace amounts of the desired products were obtained as mixtures with other products, whose structure could not be established, as judged by ^{1}H NMR spectra. We may ascribe this poor result to the decrease of reactivity towards the present acid catalyzed cyclization due to the electron-withdrawing group.

In summary, we have demonstrated that the reaction of α-substituted 2-lithio-β-methoxystyrenes with sulfur, followed by hydriodic acid mediated cyclization of the resulting α-substituted β-methoxy-2-sulfanylstyrenes provides a new and convenient method for the preparation of 3-substituted benzo[*b*]thiophenes. Although yields of the products are moderate, the present method may prove useful in organic synthesis because of some advantages; it employs readily available starting materials and is experimentally simple, and the sulfur source is inexpensive. Applications of the reaction of 2-lithiostyrene derivatives with sulfur to the preparation of other heterocyclic compounds are now in progress in our laboratory.

EXPERIMENTAL

The melting point of (2-bromo-5-methoxyphenyl)(3,4-dimethylphenyl)methanone was obtained on a Laboratory Devices MEL-TEMP II melting apparatus and is uncorrected. IR spectra were determined with a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400 FT NMR spectrometer operating at 400 MHz. The ^{13}C NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) m were measured by a JEOL JMS AX505 HA spectrometer. TLC was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 2-Bromo-β-(methoxyvinyl)styrenes (**1a**),[5] (**1b**),[6] (**1c**),[7] (**1d**),[7] 2-bromo-5-methoxybenzaldehyde,[8] and 2-bromo-4-methoxybenzaldehyde[9] were prepared by previously reported appropriate methods.

Aryl(2-bromophenyl)methanols. These compounds were prepared by reacting the respective 2-bromobenzaldehydes with the appropriate arylmagnesium bromides in THF at 0 °C.

(2-Bromo-5-methoxyphenyl)(3,4-dimethylphenyl)methanol: 89% yield; a pale-yellow oil; R_f 0.22 (1:5 Et_2O–hexane); IR (neat) 3397 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.23 (s, 3H), 2.24 (s, 3H), 2.25 (d, J = 3.7 Hz, 1H), 3.80 (s, 3H), 6.06 (d, J = 3.7 Hz, 1H), 6.71 (dd, J = 8.7, 2.7 Hz, 1H), 7.08–7.11 (m, 2H), 7.16 (s, 1H), 7.21 (d, J = 2.7 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H). Anal. Calcd for $C_{16}H_{17}BrO_2$: C, 59.83; H, 5.33. Found: C, 59.72; H, 5.39.

(2-Bromo-4-methoxyphenyl)(3-methylphenyl)methanol: 93% yield; a yellow oil; R_f 0.85 (1:5 Et_2O–hexane); IR (neat) 3391, 1605 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.27 (d, J = 3.6 Hz, 1H), 2.33 (s, 3H), 3.78 (s, 3H), 6.13 (d, J = 3.6 Hz, 1H), 6.87 (dd, J = 8.4, 2.6 Hz, 1H), 7.07–7.10 (m, 2H), 7.16–7.24 (m, 3H), 7.40 (d, J = 8.4 Hz, 1H). Anal. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92. Found: C, 58.41; H, 5.01.

(2-Bromo-4-methoxyphenyl)(4-methylphenyl)methanol: 92% yield; a pale-yellow oil; R_f 0.35 (1:5 THF–hexane); IR (neat) 3383, 1605 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.24 (d, J = 4.1 Hz, 1H), 2.33 (s, 3H), 3.79 (s, 3H), 6.12 (d, J = 4.1 Hz, 1H), 6.87 (dd, J = 8.7, 2.3 Hz, 1H), 7.08 (d, J = 2.3 Hz, 1H), 7.14 (d, J = 8.7 Hz, 1H), 7.27 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H). Anal. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92. Found: C, 58.43; H, 4.97.

Aryl(2-bromophenyl)methanones. These compounds were prepared by the PCC oxidation of the above alcohols in CH_2Cl_2 at rt.

(2-Bromo-5-methoxyphenyl)(3,4-dimethylphenyl)methanone: 73% yield; a pale-yellow solid; mp 85–86 °C (hexane–Et_2O); IR (KBr) 1659, 1601 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.31 (s, 3H), 2.33 (s, 3H), 3.80 (s, 3H), 6.85 (d, J = 3.2 Hz, 1H), 6.89 (dd, J = 9.2, 3.2 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.47–7.52

(m, 2H), 7.65 (s, 1H). Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74. Found: C, 60.18; H, 4.85.

(2-Bromo-4-methoxyphenyl)(3-methylphenyl)methanone: 81% yield; a pale-yellow oil; R_f 0.11 (1:10 Et_2O–hexane); IR (neat) 1668, 1599 cm^{-1}; ^1H NMR (500 MHz) δ 2.40 (s, 3H), 3.87 (s, 3H), 6.92 (dd, J = 8.7, 2.3 Hz, 1H), 7.19 (d, J = 2.3 Hz, 1H), 7.31 (d, J = 8.7 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 7.3 Hz, 1H), 7.55 (d, J = 7.3 Hz, 1H), 7.64 (s, 1H). Anal. Calcd for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 59.01; H, 4.28.

(2-Bromo-4-methoxyphenyl)(4-methylphenyl)methanone: 53% yield; a pale-yellow oil; R_f 0.32 (1:4 C_6H_6–hexane); IR (neat) 1667, 1605 cm^{-1}; ^1H NMR (500 MHz) δ 2.43 (s, 3H), 3.86 (s, 3H), 6.92 (dd, J = 8.7, 2.3 Hz, 1H), 7.18 (d, J = 2.3 Hz, 1H), 7.25 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 8.2 Hz, 2H). Anal. Calcd for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 58.95; H, 4.50.

1-Bromo-2-(1-aryl-2-methoxyethenyl)benzenes 1e-g. These compounds were prepared by reacting the above ketones with (methoxymethylene)triphenylphosphorane in THF at 0 °C in a manner similar to that for the preparation of **1a-d**.[5-7]

1-Bromo-4-methoxy-2-[2-methoxy-1-(3,4-dimethylphenyl)ethenyl]benzene (1e): 61% yield as a mixture of stereoisomers (*E*:*Z* = *ca*. 6:4). The analytical specimen of each isomer was obtained by fractional column chromatography on silica gel. ***E*-1e:** a colorless oil; R_f 0.32 (1:3 CH_2Cl_2–hexane); IR (neat) 1643 cm^{-1}; ^1H NMR (400 MHz) δ 2.13 (s, 3H), 2.14 (s, 3H), 3.71 (s, 3H), 3.72 (s, 3H), 6.12 (s, 1H), 6.66 (dd, J = 8.7, 3.2 Hz, 1H), 6.79 (d, J = 3.2 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 7.02 (dd, J = 8.1, 1.8 Hz, 1H), 7.11 (s, 1H), 7.38 (d, J = 8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{19}BrO_2$: C, 62.26; H, 5.52. Found: C, 62.13; H, 5.66. ***Z*-1e:** a colorless oil; R_f 0.21 (1:3 CH_2Cl_2–hexane); IR (neat) 1634 cm^{-1}; ^1H NMR (400 MHz) δ 2.20 (s, 3H), 2.21 (s, 3H), 3.72 (s, 3H), 3.76 (s, 3H), 6.61 (s, 1H), 6.73 (dd, J = 8.7, 2.6 Hz, 1H), 6.77 (d, J = 2.6 Hz, 1H), 6.84 (dd, J = 7.7, 2.2 Hz, 1H), 6.92 (s, 1H), 7.01 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H). Anal. Calcd for $C_{18}H_{19}BrO_2$: C, 62.26; H, 5.52. Found: C, 61.98; H, 5.53.

1-Bromo-5-methoxy-2-[2-methoxy-1-(3-methylphenyl)ethenyl]benzene (1f): 66% yield as a mixture of stereoisomers (*E*:*Z* = *ca*. 6:4). The analytical specimen of each isomer was obtained by fractional column chromatography on silica gel. ***E*-1f:** a pale-yellow oil; R_f 0.29 (1:10 CH_2Cl_2–hexane); IR (neat) 1634, 1601 cm^{-1}; ^1H NMR (500 MHz) δ 2.29 (s, 3H), 3.72 (s, 3H), 3.80 (s, 3H), 6.64 (s, 1H), 6.88 (dd, J = 8.2, 2.3 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.94 (s, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.128 (t, J = 7.8 Hz, 1H), 7.132 (d, J = 8.2 Hz, 1H), 7.20 (d, J = 2.3 Hz, 1H). Anal. Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.25; H, 5.34. ***Z*-1f:** a pale-yellow oil; R_f 0.14 (1:10 CH_2Cl_2–hexane); IR (neat) 1645, 1601 cm^{-1}; ^1H NMR (500 MHz) δ 2.29 (s, 3H), 3.79 (s, 3H), 3.82 (s, 3H), 6.20 (s, 1H), 6.85 (dd, J = 8.2, 2.7 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 7.14–7.16 (m, 3H), 7.20 (s, 1H), 7.20 (d, J = 8.2 Hz, 1H). Anal. Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.25; H, 5.14.

1-Bromo-5-methoxy-2-[2-methoxy-1-(4-methylphenyl)ethenyl]benzene (1g): 48% yield as a mixture of stereoisomers (*E*:*Z* = *ca*. 6:4). The analytical specimen of each isomer was obtained by fractional

column chromatography on silica gel. ***E*-1g:** a pale-yellow oil; R_f 0.20 (1:5 CH_2Cl_2–hexane); IR (neat) 1634 cm^{-1}; ^1H NMR (500 MHz) δ 2.31 (s, 3H), 3.78 (s, 3H), 3.81 (s, 3H), 6.18 (s, 1H), 6.85 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 2.7 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H). Anal. Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.24; H, 5.37. ***Z*-1g:** a pale-yellow oil; R_f 0.08 (1:5 CH_2Cl_2–hexane); IR (neat) 1643, 1601 cm^{-1}; ^1H NMR (500 MHz) δ 2.23 (s, 3H), 3.64 (s, 3H), 3.73 (s, 3H), 6.54 (s, 1H), 6.80 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 2.7 Hz, 1H). Anal. Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.09; H, 5.13.

Typical Procedure for the Preparation of Benzo[*b*]thiophenes (3). 3-Methylbenzo[*b*]thiophene (3a). To a stirred solution of **1a** (0.22 g, 0.95 mmol) in Et_2O (5 mL) at 0 ˚C was added *n*-BuLi (1.6 M solution in hexane; 1.05 mmol) dropwise. After 1 h sulfur (34 mg, 1.05 mmol) was added, and the mixture was stirred for an additional 10 min at the same temperature. Et_2O (10 mL), saturated aqueous NH_4Cl (5 mL) and water (5 mL) were added. The layers were separated and the aqueous layer was extracted with Et_2O twice (10 mL each). The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue, which was dissolved in MeCN (3 mL). After Ar gas was bubbled through this solution for 5 min, concentrated HI (0.21 g, 0.95 mmol) was added and the mixture was stirred at rt for 1 h. Saturated aqueous $NaHCO_3$ (15 mL) was added, and the organic materials were extracted with Et_2O three times (10 mL each). The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated by evaporation. The residue was purified by preparative TLC on silica gel to give **3a** (48 mg, 34%); a pale-yellow oil; R_f 0.72 (1:2 CH_2Cl_2–hexane). The spectral data of this product were identical to those reported previously.[10]

3-Phenylbenzo[*b*]thiophene (3b): a pale-yellow oil; R_f 0.50 (1:20 CH_2Cl_2–hexane). The spectral data of this product were identical to those reported previously.[10]

3-(4-*t*-Butylphenyl)benzo[*b*]thiophene (3c): a pale-yellow oil; R_f 0.52 (hexane); IR (neat) 3065 cm^{-1}; ^1H NMR (500 MHz) δ 1.39 (s, 9H), 7.36–7.40 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.90–7.96 (m, 2H); ^{13}C NMR δ 31.38, 34.64, 122.88, 123.01, 123.06, 124.21, 124.31, 125.63, 128.35, 133.11, 138.00, 138.02, 140.69, 150.51; MS *m/z* 266 (M^+, 63), 251 (100). Anal. Calcd for $C_{18}H_{18}S$: C, 81.15; H, 6.81. Found: C, 80.96; H, 6.81.

3-(4-Methoxyphenyl)benzo[*b*]thiophene (3d): a pale-yellow oil; R_f 0.49 (1:10 AcOEt–hexane). The spectral data of this product were identical to those reported previously.[8]

3-(3,4-Dimethylphenyl)-5-methoxybenzo[*b*]thiophene (3e): a pale-yellow oil; R_f 0.36 (1:10 CH_2Cl_2–hexane); IR (neat) 3013 cm^{-1}; ^1H NMR (500 MHz) δ 2.34 (s, 6H), 3.83 (s, 3H), 7.03 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.35–7.37 (m, 3H), 7.76 (d, *J* = 8,7 Hz, 1H); ^{13}C NMR δ 19.54, 19.88, 55.61, 105.40, 114.50, 123.46, 124.20, 125.90, 129.83, 130.01, 133.06, 133.72, 135.97, 137.02, 137.86, 139.15, 157.66; MS *m/z* 268 (M^+, 100). Anal. Calcd for $C_{17}H_{16}OS$: C,

76.08; H, 6.01. Found: C, 75.92; H, 6.07.

6-Methoxy-3-(3-methylphenyl)benzo[*b*]thiophene (3f): a yellow oil; R_f 0.44 (1:3 CH_2Cl_2–hexane); IR (neat) 3096, 1603 cm^{-1}; ^1H NMR (500 MHz) δ 2.43 (s, 3H), 3.86 (s, 3H), 7.01 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.20 (s, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.36–7.39 (m, 4H), 7.78 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR δ 21.49, 55.63, 105.22, 114.38, 120.53, 123.62, 125.67, 128.25, 128.58, 129.30, 132.12, 136.09, 137.85, 138.35, 142.11, 154.25; MS *m/z* 254 (M^+, 100). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.58; H, 5.78.

6-Methoxy-3-(4-methylphenyl)benzo[*b*]thiophene (3g): a colorless oil; R_f 0.24 (hexane); IR (neat) 3102, 1603 cm^{-1}; ^1H NMR (500 MHz) δ 2.42 (s, 3H), 3.88 (s, 3H), 7.00 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.17 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 2.7 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR δ 21.22, 55.61, 105.23, 114.34, 120.23, 123.58, 128.44, 129.38, 132.15, 133.25, 137.24, 137.68, 142.11, 157.47; MS *m/z* 254 (M^+, 100). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55. Found: C, 75.80; H, 5.50.

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