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SYNTHESIS OF 2-BENZOTHIOPHENE-1(3*H*)-THIONE AND ISOTHIOCHROMENE-1-THIONE DERIVATIVES BY IODINE-MEDIATED CYCLIZATION OF LITHIUM 2-(VINYL)DITHIOBENZOATE DERIVATIVES

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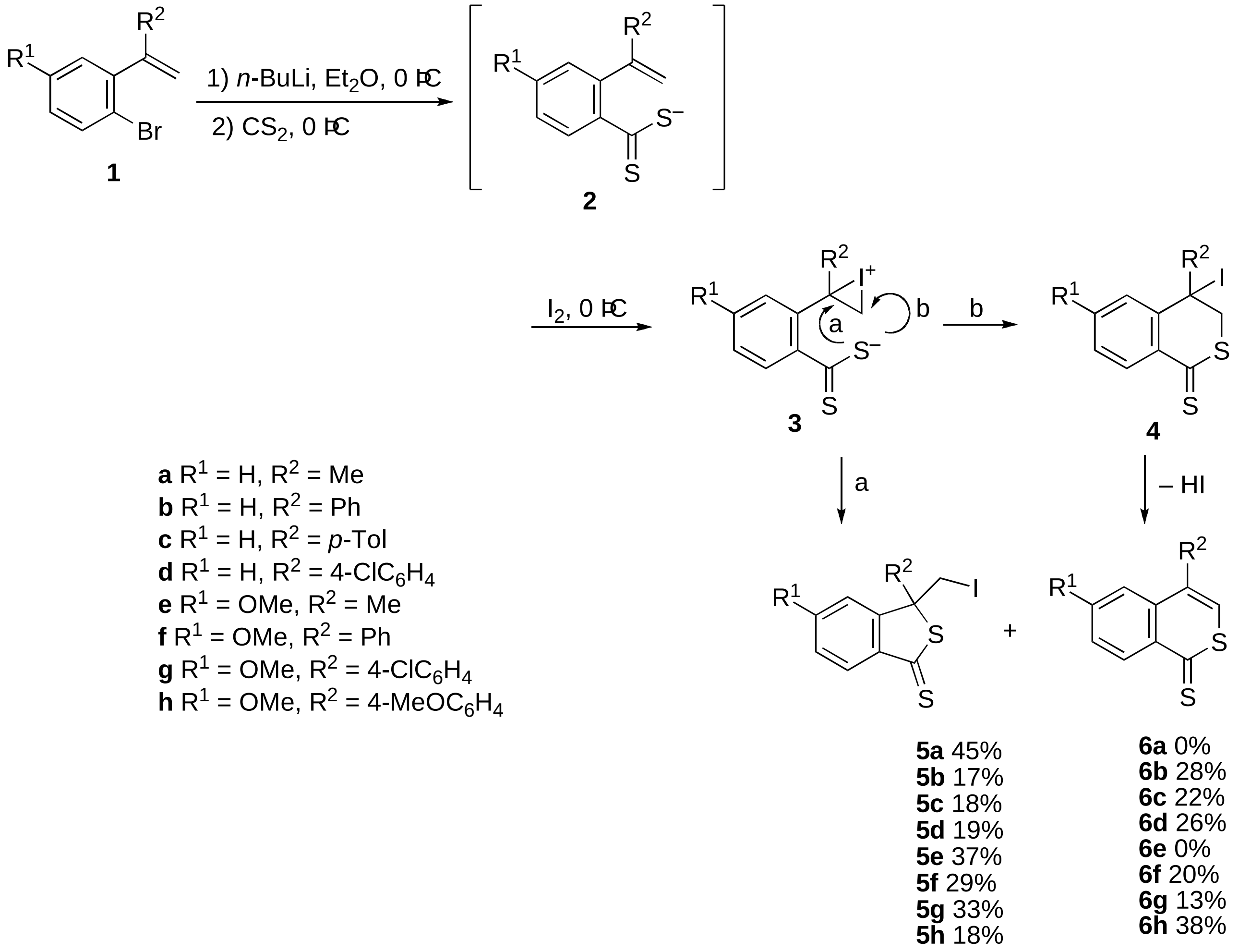
Abstract - Successive treatment of α-substituted 2-bromostyrenes with butyllithium and carbon disulfide generates lithium 2-(vinyl)dithiobenzoates, which are then allowed to react with iodine to give 3-substituted 3-iodomethyl-2-benzothiophene-1(3*H*)-thiones and/or 4-substituted isothiochromene-1-thiones in one-pot. Some of the former products can be transformed into the corresponding latter products on treatment with sodium hydrogencarbonate in refluxing acetonitrile.

INTRODUCTION

In the course of our studies on the development of new methods for the preparation of benzene-fused heterocycles utilizing iodine-mediated cyclization of appropriately *o*-substituted styrene derivatives,[1] we now wish to report a convenient method for the preparation of 2-benzothiophene-1(3*H*)-thione (**5**) and isothiochromene-1-thione derivatives (**6**) by a treatment of 2-(vinyl)dithiobenzoate derivatives (**2**) with iodine. To the best of our knowledge, this is the first report on the iodine-mediated cyclization of dithiobenzoates. These intermediates (**2**) can be generated in situ by a successive treatment of α-substituted 2-bromostyrene derivatives (**1**) with butyllithium and carbon disulfide. Therefore, the method allows one-pot access to these sulfur-containing heterocycles from **1**. Although these heterocycles, especially isothiochromene-1-thiones, may be of interest from a biological point of view, there have been a few reports on the synthesis of these classes of compounds in the literature;[2,3] the methods involve troublesome procedures, and suffer from considerably lower generality.

RESULTS AND DISCUSSION

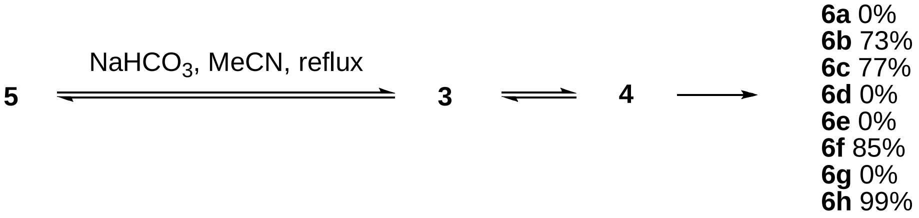
Our one-pot synthesis of 2-benzothiophene-1(3*H*)-thione (**5**) and isothiochromene-1-thione derivatives



Scheme 1

(**6**) was conducted as shown in Scheme 1. Thus, successive treatment of 2-bromostyrene derivatives (**1**) with butyllithium and carbon disulfide in diethyl ether at 0 °C generated 2-(vinyl)dithiobenzoate derivatives (**2**), which were allowed to react with iodine to give, after usual workup followed by purification using column chromatography on silica gel, **5** and/or **6** in the yields listed in Scheme 1. The former products, 3-iodomethyl-2-benzothiophene-1(3*H*)-thiones (**5**), were produced via iodine-mediated 5-*exo* ring closure (path a), and the latter products, 4-substituted isothiochromene-1-thione (**6**), were produced via iodine-mediated 6-*endo* ring closure, forming intermediate (**4**), followed by elimination of hydrogen iodide (path b). As can be seen from Scheme 1, the reactions generally afforded separable mixtures of products (**5**) and (**6**) in reasonable total yields. However, when 2-bromo-α-methylstyrene derivatives (**1a**) and (**1e**) were used as starting materials, the corresponding 2-benzothiophene-1(3*H*)-thione derivatives (**5**) were sole isolated products, and no trace of isothiochromene-1-thione derivatives (**6**) were obtained. This may be ascribed to the absence of conjugation between the 4-methyl substituent and 3,4-double bond of the isothiochromene-1-thione structure. It should be noted that the ratios of the products were unchanged even when the reactions were carried out under refluxing conditions.

Some of 3-substituted 3-iodomethyl-2-benzothiophene-1(3*H*)-thiones (**5**) proved to be transformed into the corresponding 4-substituted isothiochromene-1-thione derivatives (**6**). Thus, mixtures of **5** and sodium hydrogencarbonate in acetonitrile were heated at reflux temperature to give **6** in good yields as listed in Scheme 2. When another 3-substituent than iodomethyl was methyl or 4-chlorophenyl (*i.e.*, **5a**, **d**, **e**, and **g**), this transformation reaction did not occur and the starting materials were recovered almost quantitatively. This transformation is thought to proceed trough equilibrium between the intermediates (**4**) and (**3**), which is generated by treating **5** with sodium hydrogencarbonate. E1-like elimination of hydrogen iodide from the intermediate (**4**) gives rise to **6**. Although we have no explicit explanation of the reason for this, methyl and 4-chlorophenyl substituents may make this elimination difficult.



Scheme 2

In conclusion, a new one-pot synthesis of 2-benzothiophene-1(3*H*)-thione and isothiochromene-1-thione derivatives have been developed. Since the method employs readily available starting materials and is experimentally simple, it may be of value in organic synthesis. Work on syntheses utilizing reactions of 2-lithiostyrene derivatives with carbon disulfide and related reagents is currently in progress in our laboratory, and the results will be reported in the near future.

EXPERIMENTAL

The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. The ^{1}H NMR spectra were determined in $CDCl_3$ using $SiMe_4$ as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. The ^{13}C NMR spectrum was 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) were measured by a JEOL JMS-AX505 HA spectrometer. Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 PF_{254}. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the solvents used were dried over appropriate drying agents and distilled under argon prior to use.

Starting Materials. 1-Bromo-2-(1-methylethenyl)benzene (**1a**),[4] 1-bromo-2-(1-phenylethenyl)benzene (**1b**),[5] 2-bromophenyl(4-methylphenyl)methanone,[6] 1-bromo-2-[1-(4-chlorophenyl)ethenyl]benzene (**1d**),[1a] 1-bromo-4-methoxy-2-(1-methylethenyl)benzene (**1e**),[7] 1-bromo-4-methoxy-2-(1-phenylethenyl)benzene (**1f**),[6] and 2-bromo-5-methoxybenzaldehyde[4] were prepared by the appropriate reported procedures. All other chemicals used in this study were commercially available.

1-Bromo-2-[1-(4-methylphenyl)ethenyl]benzene (1c). This compound was prepared by the reaction of 2-bromophenyl(4-methylphenyl)methanone[6] with methylenetriphenylphosphorane in THF at 0 ˚C in 81% yield; a colorless oil; R_f 0.50 (hexane); IR (neat) 1614 cm^{-1}; ^{1}H NMR δ 2.34 (3H, s), 5.20 (1H, s), 5.80 (1H, s), 7.11 (2H, d, J = 8.2 Hz), 7.16 (2H, d, J = 8.2 Hz), 7.20 (1H, ddd, J = 7.8, 7.3, 1.8 Hz), 7.30 (1H, dd, J = 7.3, 1.8 Hz), 7.34 (1H, td, J = 7.3, 1.4 Hz), 7.59 (1H, d, J = 7.8 Hz). Anal. Calcd for $C_{15}H_{13}Br$: C, 65.95; H, 4.80. Found: C, 65.92; H, 5.00.

2-Bromo-5-methoxyphenyl(4-chlorophenyl)methanol. This compound was prepared by the reaction of 2-bromo-5-methoxybenzaldehyde[4] with 4-chlorophenylmagnesium bromide in THF at 0 ˚C in 92% yield; a pale-yellow oil; R_f 0.39 (1:2 Et_2O–hexane); IR (neat) 3366 cm^{-1}; ^{1}H NMR δ 2.35 (1H, d, J = 3.7 Hz), 3.79 (3H, s), 6.12 (1H, d, J = 3.7 Hz), 6.73 (1H, dd, J = 8.7, 3.2 Hz), 7.12 (1H, d, J = 3.2 Hz), 7.30 (2H, d, J = 8.7 Hz), 7.34 (2H, d, J = 8.7 Hz), 7.42 (1H, d, J = 8.7 Hz). Anal. Calcd for $C_{14}H_{12}BrClO_2$: C, 51.33; H, 3.69. Found: C, 51.32; H, 3.42.

2-Bromo-5-methoxyphenyl(4-chlorophenyl)methanone. This compound was prepared by the PCC oxidation of 2-bromo-5-methoxyphenyl(4-chlorophenyl)methanol in 1,2-dichloroethane at rt in 77% yield; a white solid; mp 76–78 ˚C (hexane); IR (KBr) 1668 cm^{-1}; ^{1}H NMR δ 3.81 (3H, s), 6.86 (1H, d, J = 3.2 Hz), 6.92 (1H, dd, J = 8.7, 3.2 Hz), 7.44 (2H, d, J = 8.7 Hz), 7.52 (1H, d, J = 8.7 Hz), 7.76 (2H, d, J = 8.7 Hz). Anal. Calcd for $C_{14}H_{10}BrClO_2$: C, 51.65; H, 3.10. Found: C, 51.55; H, 3.13.

1-Bromo-2-[1-(4-chlorophenyl)ethenyl]-4-methoxybenzene (1g). This compound was prepared by treating 2-bromo-5-methoxyphenyl(4-chlorophenyl)methanone with methylenetriphenylphosphorane in THF at 0 ˚C in 90% yield; a pale-yellow oil; R_f 0.61 (1:5 Et_2O–hexane); IR (neat) 1589 cm^{-1}; ^{1}H NMR δ 3.81 (3H, s), 5.28 (1H, s), 5.80 (1H, s), 6.78 (1H, dd, J = 8.7, 3.2 Hz), 6.85 (1H, d, J = 3.2 Hz), 7.20 (2H, d, J = 8.7 Hz), 7.27 (2H, d, J = 8.7 Hz), 7.46 (1H, d, J = 8.7 Hz). Anal. Calcd for $C_{15}H_{12}BrClO$: C, 55.67; H, 3.74. Found: C, 55.62; H, 3.75.

2-Bromo-5-methoxyphenyl(4-methoxyphenyl)methanol. This compound was prepared by the reaction of 2-bromo-5-methoxybenzaldehyde[4] with 4-methoxyphenylmagnesium bromide in THF at 0 ˚C in 90% yield; a white solid; mp 83–84 ˚C (hexane–Et_2O); IR (KBr) 3400, 1611 cm^{-1}; ^{1}H NMR δ 2.26 (1H, d, J = 3.8 Hz), 3.79 (3H, s), 3.80 (3H, s), 6.07 (1H, d, J = 3.8 Hz), 6.71 (1H, dd, J = 8.4, 3.1 Hz), 6.86 (2H, d, J = 8.4 Hz), 7.22 (1H, d, J = 3.1 Hz), 7.31 (2H, d, J = 8.4 Hz), 7.40 (1H, d, J = 8.4 Hz). Anal. Calcd for $C_{15}H_{15}BrO_3$: C, 55.75; H, 4.68. Found: C, 55.50; H, 4.50.

2-Bromo-5-methoxyphenyl(4-methoxyphenyl)methanone. This compound was prepared by the PCC oxidation of 2-bromo-5-methoxyphenyl(4-methoxyphenyl)methanol in 1,2-dichloroethane at rt in 84% yield; colorless needles; mp 71–73 °C (hexane); IR (KBr) 1653, 1603 cm^{-1}; ^{1}H NMR δ 3.80 (3H, s), 3.88 (3H, s), 6.85 (1H, d, *J* = 2.7 Hz), 6.89 (1H, dd, *J* = 8.7, 2.7 Hz), 6.94 (2H, d, *J* = 9.2 Hz), 7.50 (1H, d, *J* = 8.7 Hz), 7.81 (2H, d, *J* = 9.2 Hz). Anal. Calcd for $C_{15}H_{13}BrO_3$: C, 56.10; H, 4.08. Found: C, 55.76; H, 4.35.

1-Bromo-4-methoxy-2-[1-(4-methoxyphenyl)ethenyl]benzene (1h). This compound was prepared by treating 2-bromo-5-methoxyphenyl(4-methoxyphenyl)methanone with methylenetriphenylphosphorane in THF at 0 °C in 92 % yield; a colorless oil; R_f 0.32 (1:10 THF–hexane); IR (neat) 1606 cm^{-1}; ^{1}H NMR δ 3.80 (6H, s), 5.15 (1H, s), 5.73 (1H, s), 6.77 (1H, dd, *J* = 8.7, 3.2 Hz), 6.83 (2H, d, *J* = 9.2 Hz), 6.86 (1H, d, *J* = 3.2 Hz), 7.21 (2H, d, *J* = 9.2 Hz), 7.46 (1H, d, *J* = 8.7 Hz). Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74. Found: C, 60.25; H, 4.55.

Typical Procedure for the Preparation of 2-Benzothiophene-1(3*H*)-thione (5) and 1*H*-2-Benzothiopyran-1-thione Derivatives (6). 3-Iodomethyl-3-phenyl-2-benzothiophene-1(3*H*)-thione (5b) and 4-Phenyl-1*H*-2-benzothiopyran-1-thione (6b). To a stirred solution of **1b** (0.52 g, 2.0 mmol) in Et_2O (6 mL) at 0 °C was added *n*-BuLi (1.6 M in hexane; 2.2 mmol) (1 M = 1 mol dm^{-3}) dropwise; the mixture was stirred for 1 h. To the resulting mixture CS_2 (0.18 g, 2.4 mmol) was added. After 15 min, I_2 (1.0 g, 4.0 mmol) was added and stirring was continued for an additional 2 h at the same temperature before 10% aqueous $Na_2S_2O_3$ was added until the color of iodine disappeared. The mixture was diluted with Et_2O (6 mL) and the layers were separated. The aqueous layer was extracted with Et_2O twice (5 mL each), and the combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel to afford **5b** (0.13 g, 17%) and **6b** (0.14 g, 28%). **5b:** a red oil; R_f 0.32 (1:10 THF–hexane); IR (neat) 1269, 1051 cm^{-1}; ^{1}H NMR δ 4.23 (1H, d, *J* = 10.5 Hz), 4.31 (1H, d, *J* = 10.5 Hz), 7.30–7.40 (6H, m), 7.53 (1H, ddd, *J* = 7.8, 7.3, 0.9 Hz), 7.66 (1H, td, *J* = 7.3, 1.4 Hz), 8.06 (1H, d, *J* = 7.3 Hz); MS *m/z* 382 (M$^+$, 33), 255 (100). HR-MS Calcd for $C_{15}H_{11}IS_2$: M, 381.9347. Found: *m/z* 381.9370. **6b:** red needles; mp 101–103 °C (hexane); IR (KBr) 1217, 1009 cm^{-1}; ^{1}H NMR δ 7.05 (1H, s), 7.36 (2H, dd, *J* = 7.8, 1.4 Hz), 7.44–7.53 (4H, m), 7.60 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 7.67 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 9.02 (1H, dd, *J* = 7.8, 1.4 Hz); ^{13}C NMR δ 128.05, 128.33, 128.66, 128.73, 129.20, 129.33, 129.37, 132.20, 133.79, 137.18, 137.64, 138.97, 210.53; MS *m/z* 254 (M$^+$, 100). Anal. Calcd for $C_{15}H_{10}S_2$: C, 70.83; H, 3.96. Found: C, 70.64; H, 4.09.

3-Iodomethyl-3-methyl-2-benzothiophene-1(3*H*)-thione (5a): a red oil; R_f 0.33 (1:5 Et_2O–hexane); IR (neat) 1271, 1049 cm^{-1}; ^{1}H NMR δ 2.05 (3H, s), 3.74 (1H, d, *J* = 10.5 Hz), 3.83 (1H, d, *J* = 10.5 Hz), 7.48 (1H, d, *J* = 7.8 Hz), 7.50 (1H, dd, *J* = 7.8, 7.3 Hz), 7.69 (1H, dd, *J* = 7.8, 7.3 Hz), 8.00 (1H, d, *J* = 7.8 Hz); ^{13}C NMR δ 16.18, 27.47, 64.86, 122.93, 125.01, 129.40, 133.05, 142.94, 151.96, 225.07; MS *m/z* 320 (M$^+$, 35), 193 (100). HR-MS Calcd for $C_{10}H_9IS_2$: M, 319.9190. Found: *m/z* 319.9185.

3-Iodomethyl-3-(4-methylphenyl)-2-benzothiophene-1(3*H*)-thione (5c): a red oil; R_f 0.32 (1:10 THF–hexane); IR (neat) 1269, 1051 cm^{-1}; ^{1}H NMR δ 2.34 (3H, s), 4.21 (1H, d, *J* = 11.0 Hz), 4.29 (1H, d, *J* = 11.0 Hz), 7.15 (2H, d, *J* = 7.8 Hz), 7.27 (2H, d, *J* = 7.8 Hz), 7.37 (1H, d, *J* = 7.8 Hz), 7.52 (1H, ddd, *J* = 7.8, 7.3, 0.9 Hz), 7.64 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 8.05 (1H, d, *J* = 7.8 Hz); MS *m/z* 396 (M$^+$, 35), 269 (100). HR-MS Calcd for $C_{16}H_{13}IS_2$: M, 395.9503. Found: *m/z* 395.9495.

4-(4-Methylphenyl)-1*H*-2-benzothiopyran-1-thione (6c): red needles; mp 136–138 ˚C (hexane); IR (KBr disk) 1219, 1007 cm^{-1}; ^{1}H NMR δ 2.44 (3H, s), 7.03 (1H, s), 7.25 (2H, d, *J* = 8.2 Hz), 7.29 (2H, d, *J* = 8.2 Hz), 7.55 (1H, dd, *J* = 7.8, 1.4 Hz), 7.60 (1H, ddd, *J* = 8.2, 6.9, 1.4 Hz), 7.66 (1H, ddd, *J* = 7.8, 6.9, 1.4 Hz), 9.01 (1H, dd, *J* = 8.2, 1.4 Hz); MS *m/z* 268 (M$^+$, 100). Anal. Calcd for $C_{16}H_{12}S_2$: C, 71.60; H, 4.51. Found: C, 71.42; H, 4.80.

3-(4-Chlorophenyl)-3-iodomethyl-2-benzothiophene-1(3*H*)-thione (5d): a red solid; mp 53–55 ˚C (pentane); IR (KBr) 1267, 1051 cm^{-1}; ^{1}H NMR δ 4.19 (1H, d, *J* = 10.5 Hz), 4.25 (1H, d, *J* = 10.5 Hz), 7.33 (4H, s), 7.52–7.56 (2H, m), 7.66 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 8.05 (1H, d, *J* = 7.8 Hz); MS *m/z* 416 (M$^+$, 34), 269 (100). Anal. Calcd for $C_{15}H_{10}ClIS_2$: C, 43.23; H, 2.42. Found: C, 42.96; H, 2.52.

4-(4-Chlorophenyl)-1*H*-2-benzothiopyran-1-thione (6d): red needles; mp 113–115 ˚C (hexane–Et_2O); IR (KBr) 1217, 1009 cm^{-1}; ^{1}H NMR δ 7.03 (1H, s), 7.31 (2H, d, *J* = 8.7 Hz), 7.45–7.48 (3H, m), 7.62 (1H, ddd, *J* = 7.8, 7.3, 1.4 Hz), 7.68 (1H, ddd, *J* = 8.2, 7.3, 1.8 Hz), 9.01 (1H, dd, *J* = 8.2, 1.4 Hz); MS *m/z* 288 (M$^+$, 100). Anal. Calcd for $C_{15}H_9ClS_2$: C, 62.38; H, 3.14. Found: C, 62.37; H, 3.22.

3-Iodomethyl-5-methoxy-3-methyl-2-benzothiophene-1(3*H*)-thione (5e): a red solid; mp 103 ˚C (decomp) (pentane); IR (KBr) 1283, 1047 cm^{-1}; ^{1}H NMR δ 2.02 (3H, s), 3.72 (1H, d, *J* = 10.5 Hz), 3.78 (1H, d, *J* = 10.5 Hz), 3.93 (3H, s), 6.90 (1H, d, *J* = 2.3 Hz), 7.01 (1H, dd, *J* = 8.7, 2.3 Hz), 7.94 (1H, d, *J* = 8.7 Hz); MS *m/z* 350 (M$^+$, 55), 223 (100). Anal. Calcd for $C_{11}H_{11}IOS_2$: C, 37.72; H, 3.17. Found: C, 37.68; H, 3.22.

3-Iodomethyl-5-methoxy-3-phenyl-2-benzothiophene-1(3*H*)-thione (5f): a red solid; mp 46–48 ˚C (pentane); IR (KBr) 1279, 1055 cm^{-1}; ^{1}H NMR δ 3.87 (3H, s), 4.22 (1H, d, *J* = 11.0 Hz), 4.25 (1H, d, *J* = 11.0 Hz), 6.80 (1H, d, *J* = 2.3 Hz), 7.04 (1H, dd, *J* = 8.7, 2.3 Hz), 7.31–7.40 (5H, m), 8.00 (1H, d, *J* = 8.7 Hz); MS *m/z* 412 (M$^+$, 38), 285 (100). Anal. Calcd for $C_{16}H_{13}IOS_2$: C, 46.61; H, 3.18. Found: C, 46.80; H, 3.09.

6-Methoxy-4-phenyl-1*H*-2-benzothiopyran-1-thione (6f): red needles; mp 170–172 ˚C (hexane–Et_2O); IR (KBr) 1234, 1003 cm^{-1}; ^{1}H NMR δ 3.77 (3H, s), 6.89 (1H, d, *J* = 2.7 Hz), 7.05 (1H, s), 7.17 (1H, dd, *J* = 9.2, 2.7 Hz), 7.36 (2H, dd, *J* = 7.8, 1.4 Hz), 7.45–7.50 (3H, m), 9.03 (1H, d, *J* = 9.2 Hz); MS *m/z* 284 (M$^+$, 100). Anal. Calcd for $C_{16}H_{12}OS_2$: C, 67.57; 4.25. Found: C, 67.51; H, 4.28.

3-(4-Chlorophenyl)-3-iodomethyl-5-methoxy-2-benzothiophene-1(3*H*)-thione (5g): an orange solid; mp 47–48 ˚C (pentane); IR (KBr) 1285, 1055 cm^{-1}; ^{1}H NMR δ 3.87 (3H, s), 4.17 (1H, d, *J* = 11.4 Hz), 4.19 (1H, d, *J* = 11.4 Hz), 6.77 (1H, s), 7.05 (1H, d, *J* = 8.7 Hz), 7.33 (4H, s), 7.99 (1H, d, *J* = 8.7 Hz);

^{13}C NMR δ 13.28, 56.45, 68.68, 109.77, 116.23, 127.08, 128.53, 128.95, 129.14, 134.40, 137.22, 154.48, 164.44, 222.37; MS *m/z* 446 (M$^+$, 35), 319 (100). Anal. Calcd for $C_{16}H_{12}ClIOS_2$: C, 43.02; 2.71. Found: C, 43.16; H, 2.96.

4-(4-Chlorophenyl)-6-methoxy-1*H*-2-benzothiopyran-1-thione (6g): an orange solid; mp 147–149 ˚C (hexane–CH_2Cl_2); IR (KBr) 1234, 1001 cm^{-1}; ^{1}H NMR δ 3.79 (3H, s), 6.81 (1H, d, *J* = 2.7 Hz), 7.03 (1H, s), 7.18 (1H, dd, *J* = 9.2, 2.7 Hz), 7.31 (2H, d, *J* = 8.7 Hz), 7.47 (2H, d, *J* = 8.7 Hz), 9.02 (1H, d, *J* = 9.2 Hz); ^{13}C NMR δ 55.68, 111.04, 117.54, 129.06, 129.60, 130.57, 131.86, 132.50, 134.40, 134.50, 136.01, 137.41, 164.37, 207.96; MS *m/z* 318 (M$^+$, 100). Anal. Calcd for $C_{16}H_{11}ClOS_2$: C, 60.27; 3.48. Found: C, 60.29; H, 3.49.

3-Iodomethyl-5-methoxy-3-(4-methoxyphenyl)-2-benzothiophene-1(3*H*)-thione (5h): an orange solid; mp 45–47 ˚C (pentane); IR (KBr) 1281, 1032 cm^{-1}; ^{1}H NMR δ 3.81 (3H, s), 3.86 (3H, s), 4.19 (1H, d, *J* = 11.0 Hz), 4.22 (1H, d, *J* = 11.0 Hz), 6.79 (1H, d, *J* = 2.3 Hz), 6.87 (2H, d, *J* = 8.7 Hz), 7.03 (1H, dd, *J* = 8.7, 2.3 Hz), 7.30 (2H, d, *J* = 8.7 Hz), 7.99 (1H, d, *J* = 8.7 Hz); MS *m/z* 442 (M$^+$, 10), 314 (100). Anal. Calcd for $C_{17}H_{15}IO_2S_2$: C, 46.16; 3.42. Found: C, 46.03; H, 3.60.

6-Methoxy-4-(4-methoxyphenyl)-1*H*-2-benzothiopyran-1-thione (6h): an orange solid; mp 179–180 ˚C (hexane–CH_2Cl_2); IR (KBr) 1234, 1001 cm^{-1}; ^{1}H NMR δ 3.78 (3H, s), 3.88 (3H, s), 6.93 (1H, d, *J* = 2.7 Hz), 7.00 (2H, d, *J* = 8.7 Hz), 7.03 (1H, s), 7.16 (1H, dd, *J* = 9.2, 2.7 Hz), 7.28 (2H, d, *J* = 8.7 Hz), 9.03 (1H, d, *J* = 9.2 Hz); MS *m/z* 314 (M$^+$, 34), 269 (100). Anal. Calcd for $C_{17}H_{14}O_2S_2$: C, 64.94; 4.49. Found: C, 65.29; H, 4.23.

Typical procedure for the Transformation of 3-Iodomethyl-2-benzothiophene-1(3*H*)-thione derivatives (5) into 1*H*-2-benzothiopyran-1-thione derivatives (6). A mixture of **5b** (99 mg, 0.26 mmol) and $NaHCO_3$ (44 mg, 0.52 mmol) in MeCN (4 mL) was heated at reflux temperature. The progress of the reaction was monitored by TLC on silica gel (1:10 THF–hexane). After the complete consumption of the starting material (*ca.* 3 h), the resulting mixture was worked up in a manner similar to that described for the preparation of **5b** and **6b**. Purification of the crude product by column chromatography on silica gel (1:10 THF–hexane) gave **6b** (48 mg, 73%).

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