Pergamon

Tetrahedron 58 (2002) 4529–4533

TETRAHEDRON

A convenient synthesis of benzothiophene derivatives☆

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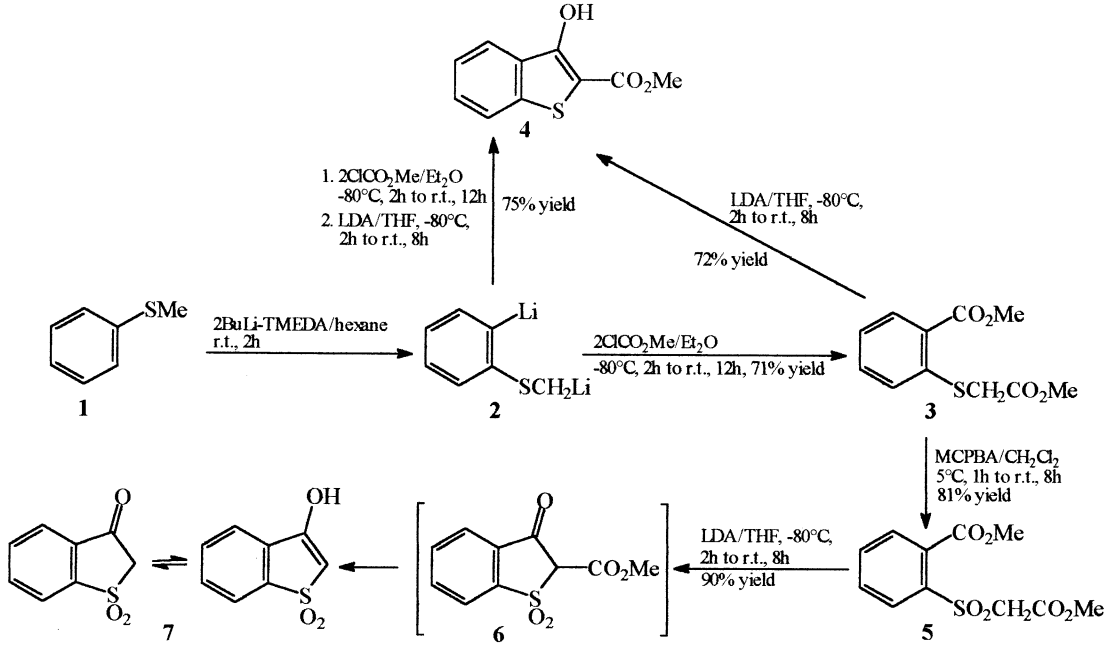
Received 24 January 2002; revised 8 March 2002; accepted 4 April 2002

Abstract—(Methylthio)- and 2-bromo-1-(methylthio)benzene are useful synthons to prepare monometallated and bimetallated intermediates which lead to 1-benzothiophenes functionalized in the three and/or two positions.

Thiophene and 1-benzothiophene compounds have been detected in coal tar, bituminous coal, shale oil and some Middle Eastern oil. Various derivatives have been found in plants, coffee and solid particulate matter in city air presumably coming from coal-fired furnaces.[2,3] The 1-benzothiophenic nucleus has been widely used, during the first half of the 20th century, for the synthesis of thioindigo dyes.[2,3] 1-Benzothiophenes show pesticidal activity, and, furthermore, pharmacological properties as antibiotics, analgesics, antiexudatives, antiinflammatories, diuretics and enzyme inhibitors.[2,3]

In previous works we showed that (methylthio)- and (isopropylsulfonyl)- arenes are useful synthons to prepare 1,2-disubstituted benzenes in one-step and one-pot with the same or different groups.[4–6] These results led us to look for



Scheme 1.

☆ See Ref. 1.

Keywords: 1-benzothiophenes; thioethers; metallation; lithiation.

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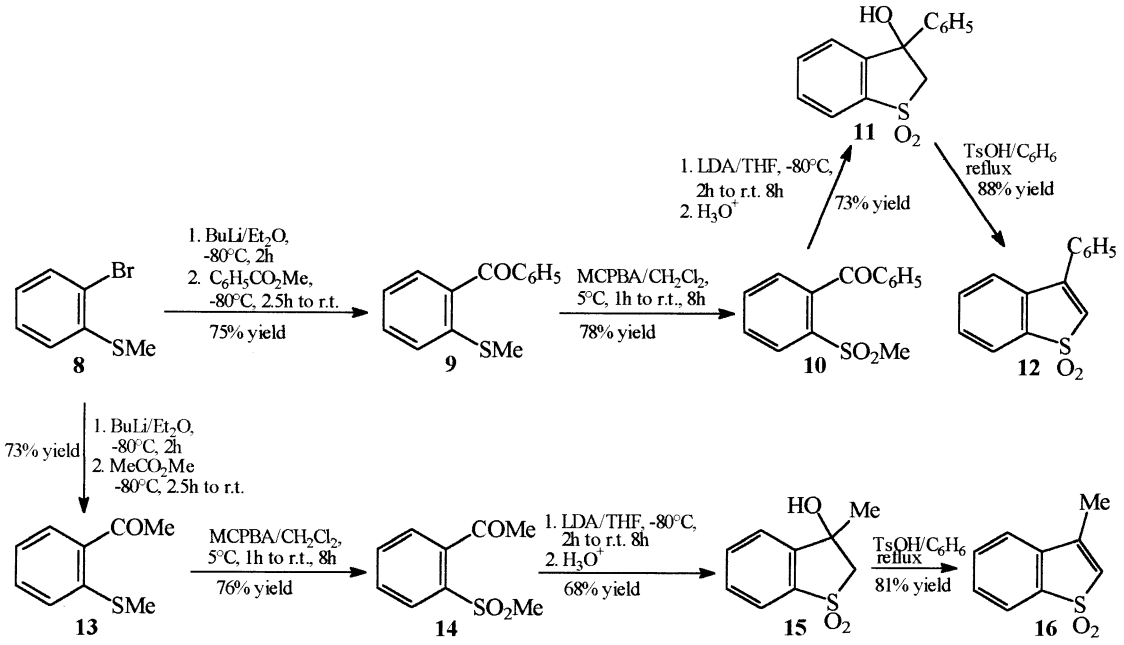
0040–4020/02/$ - see front matter
PII: S0040-4020(02)00399-X



Scheme 2.

new synthetic one-pot paths to 3- and 2,3-disubstituted 1-benzothiophenes bearing various functional groups (hydroxy, carboxy and carbonyl). The literature often reports long and tedious processes employing very toxic reagents and requiring the isolation and purification of all intermediate compounds.[2,7–10] The peroxide-promoted thermal reaction of diphenyl disulfide with alkynes,[11] the metallation-induced cyclization of acetylenes[12] and our previous studies[13] led only to 3- or 2,3-alkyl and/or aryl substituted benzothiophenes.

We took advantage of the easy availability of the bimetallated **2** starting from commercial (methylthio)benzene (**1**).[4] Aryllithium **2**, when treated with two molar equivalents of methyl chlorocarbonate, led to the diester **3**, which, without isolation, was converted into **4** with a yield of 75% through an anionic one-pot cyclization with lithium diisoproylamide (LDA) (Scheme 1). When **3** was isolated and then cyclized the product **4** was obtained in an overall yield of 51%. When the diester **3** was isolated and oxidized to sulfone **5**, its anionic cyclization gave **7** by a rapid decarboxylation of **6** (Scheme 1).

The 2-bromo(methylthio)benzene (**8**) is revealed as a valuable synthon to prepare 1-benzothiophenes 1,1-dioxide. In fact **8** was converted into the ketone **9** through a metal–halogen exchange with butyllithium followed by quenching with methyl benzoate. The intermediate **9** was then oxidized to the sulfone **10** and converted into the benzothiophene 1,1-dioxide **11** through an anionic cyclization with LDA. After dehydration **11** gave **12**. Analogously we prepared 3-hydroxy-3-methyl-1-benzothiophene-1,1-dioxide (**15**) and 3-methyl-1-benzothiophene-1,1-dioxide (**16**) (Scheme 2).

It is remarkable that this method allows the synthesis of 3-hydroxy derivatives **11** and **15** and 3-alkyl or 3-aryl-substituted 1-benzothiophenes 1,1-dioxide with good yields and few steps. This is in contrast to all literature methods describing the acid-catalyzed cyclization of arylthioacetones or arylphenacylsulfides, which always lead to mixtures of 2- or 3-substituted isomers due to rearrangement reactions, or other methods involving many steps and lower overall yields.[2,9,14–18]

1. Experimental

1.1. General

Reagent-grade commercially available reagents and solvents were used. (Methylthio)benzene (**1**) and 1-bromo-2-(methylthio)benzene (**8**) were commercial products (Aldrich Chemical Co.). Solutions of butyllithium in hexane were purchased from Aldrich Chemical Co. and were analyzed by the Gilman double titration method.[19] Solutions of LDA in tetrahydrofuran were prepared by literature methods.[20] *N*,*N*,*N*′,*N*′-Tetramethyl-1,2-diaminoethane (TMEDA) was obtained from the Aldrich Chemical Co. and distilled from calcium hydride before use. All solvents were dried and purified using standard techniques. Petroleum ether (bp 40–70°C) was used for chromatography.

The reactions were monitored by TLC prior to workup. Solvents were evaporated from the reaction mixtures at 40°C with a rotavapor. TLC was run on silica gel plates 60 F_{254} (Merck) and visualized with UV fluorescence (254 and 366 nm). Flash chromatography was performed on silica gel 60, 0.04–0.063 mm (Fluka). Melting points were determined with a Kofler hot stage microscope and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1310 grating spectrophotometer using NaCl plates. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer. Chemical shifts are given as δ values from internal TMS. Mass spectra were obtained at 70 eV with a Hewlett–Packard 5989A mass spectrometer, using the

direct-inlet system. Microanalyses were carried out on a Carlo Erba 1106 element analyzer.

1.1.1. Methyl 3-hydroxy-1-benzothiophene-2-carboxylate (4). To a vigorously stirred solution of **1** (4.96 g, 40 mmol) and anhydrous TMEDA (9.12 g, 88 mmol) in anhydrous hexane (50 mL), a 1.2 M solution of butyllithium in hexane (37 mL, 49.5 mmol) was added under argon over a few s, and stirring was continued at 40°C for 15 min. An additional amount of butyllithium in hexane (37 mL, 49.5 mmol) was then added and the mixture was heated at 55–58°C for 1 h. The mixture was then cooled to −80°C and a solution of methyl chloroformate (7.56 g, 80 mmol) in anhydrous diethyl ether (20 mL) was gradually added under argon. The resultant mixture was stirred at −80°C for 2 h, and treated dropwise with a solution of LDA (40 mmol) in dry tetrahydrofuran (20 mL). After the addition was complete, stirring was continued for 2 h at the same temperature (−80°C). The mixture was then allowed to warm to room temperature with stirring, and then poured into water (50 mL). The pH was adjusted to 4–5 by addition of 10% aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer extracted with diethyl ether (2×20 mL). The organic phases were combined, dried (Na_2SO_4), and concentrated. The crude product was crystallized from 1/1 aqueous EtOH as white crystals. Yield 75%; mp 106–108°C (Lit.[8] mp 106.5–108°C). IR (nujol, cm^{-1}): 3264 (OH), 1669 (C═O). ^1H NMR ($CDCl_3$) δ: 4.00 (s, 3H, OCH_3), 7.65 (m, 4H, Ar-*H*), 10.18 (s, 1H, O*H*, D_2O exchangeable). ^{13}C NMR ($CDCl_3$) δ: 52.15 (*C*H_3), 101.62, 122.96, 123.12, 124.42, 128.86, 130.33, 138.79, 159.52 (*C*–OH), 167.62 (*C*O). EI-MS *m/z*: 208 (34%, M^+), 177 (17%), 176 (100%), 148 (13%), 121 (15.5%), 120 (54%), 104 (14%), 91 (17%), 85 (20%), 83 (27%), 77 (21%), 71 (17%), 69 (24%), 57 (32%), 55 (21.5%), 51 (13%). Anal calcd for $C_{10}H_8O_3S$: C, 57.68; H, 3.87; S, 15.40%. Found: C, 57.59; H, 3.81; S, 15.28.

1.1.2. Methyl 2-[(2-methoxy-2-oxoethyl)thio]benzoate (3). This compound was obtained when the above reaction mixture was quenched before the treatment with LDA. The crude product was purified by flash-chromatography on silica gel (10/1 petroleum ether/diethyl ether). Yield 71%; crystallized from 1/1 aqueous EtOH as white crystals, mp 40–42°C. IR (nujol, cm^{-1}): 1746 and 1792 (CO). ^1H NMR ($CDCl_3$) δ: 3.64 (s, 6H, OCH_3), 3.83 (s, 2H, SCH_2), 7.00 (m, 1H, Ar-*H*), 7.30 (m, 2H, Ar-*H*), 7.81 (m, 1H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 34.65 (SCH_2), 52.12 (OCH_3), 52.60 (OCH_3), 124.61, 125.80, 127.62, 131.27, 132.58, 139.98, 166.64 (CO), 169.85 (CO). EI-MS *m/z*: 240 (19%, M^+,), 208 (63%), 181 (19%), 167 (15%), 164 (16%), 149 (61.5%), 121 (15%), 108 (11.5%), 77 (10%), 59 (11.5%), 45 (100%). Anal calcd for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.03; S, 13.34%. Found: C, 54.91; H, 4.97; S, 13.21.

The product **3** was converted into **4** by treatment with one molar equivalent of LDA in the same manner as described above. Yield 72%; mp 106–108°C. Spectral data were identical to those of the above product.

1.1.3. Methyl 2-[(2-methoxy-2-oxoethyl)sulfonyl]benzoate (5). To a vigorously stirred solution of **3** (4 g, 20 mmol) in dichloromethane (150 mL) 3-chloroperbenzoic acid (8.6 g, 50 mmol)) was gradually added at 5–10°C. After the addition was complete, stirring was continued for 2 h at the same temperature. The mixture was then allowed to warm to room temperature, heated with stirring at about 40–45°C for 8 h and then filtered, washed with 10% aqueos sodium bicarbonate (3×20 mL) and dried (Na_2SO_4). Evaporation of the solvent was followed by flash-chromatography on silica gel (2/1 petroleum ether/diethyl ether). Yield 74%, crystallized from EtOH as white crystals, mp 98–100°C. IR (nujol, cm^{-1}): 1745 and 1725 (C═O), 1325 and 1150 (SO_2). ^1H NMR ($CDCl_3$) δ: 3.73 (s, 3H, $CH_2CO_2CH_3$), 3.98 (s, 3H, $ArCO_2CH_3$), 4.66 (s, 2H, $CH_2CO_2CH_3$), 7.70 (m, 3H, Ar-*H*), 8.27 (m, 1H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 52.96 ($CH_2CO_2CH_3$), 53.32 (CO_2CH_3), 60.81 ($CH_2CO_2CH_3$), 129.96, 131.13, 131.68, 132.96, 133.97, 137.74, 163.23 ($CH_2CO_2CH_3$ or $ArCO_2CH_3$), 167.24 ($CH_2CO_2CH_3$ or $ArCO_2CH_3$). EI-MS *m/z*: 241 (25%, M^+-OCH_3,), 209 (86%), 199 (43%), 176 (39%), 149 (75%), 148 (88%), 135 (75%), 104 (23%), 92 (26%), 77 (100%), 76 (46%), 50 (35%), 44 (34%). Anal calcd for $C_{11}H_{12}O_6S$: C, 48.53; H, 4.44; S, 11.77%. Found: C, 48.44; H, 4.37; S, 11.60.

1.1.4. 3-Hydroxy-1-benzothiophene-1,1-dioxide (7). A solution of **5** (2 g, 7.3 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise into a solution of LDA (7.4 mmol) in anhydrous tetrahydrofuran (10 mL). After the addition was complete the mixture was worked up in the same manner described for **4**. The crude product was crystallized from 1/1 aqueous EtOH as white crystals. Yield 90%; mp 133–134°C (Lit.[9] mp 132–134°C). IR (nujol, cm^{-1}): 1700 (CO), 1330 and 1140 (SO_2). ^1H NMR ($CDCl_3$) δ: 1.25 (s, 2H, CH_2), 7.43 (t, 1H, Ar-*H*), 7.60 (d, 1H, Ar-*H*), 8.01 (d, 1H, Ar-*H*), 8.10 (s, 1H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 29.69 (*C*H_2), 128.32, 129.85, 130.27, 130.93, 133.90, 134.72, 170.58 (CO). EI-MS *m/z*: 182 (67%, M^+), 152 (5.5%), 118 (85%), 104 (15%), 90 (100%), 89 (61%), 76 (57%), 63 (28%), 50 (63%), 39 (17%). Anal calcd for $C_8H_6O_3S$: C, 52.74; H, 3.32; S, 17.60%. Found: C, 52.63; H, 3.28; S, 17.49.

1.1.5. [2-(Methylthio)phenyl](phenyl)methanone (9). To a vigorously stirred solution of **8** (2 g, 9.8 mmol) in anhydrous diethyl ether (20 mL) a 1.2 M solution of butyllithium in hexane (7.3 mL, 9.8 mmol) was added dropwise under argon at −25°C and stirring was continued at the same temperature for 0.5 h. The mixture was then cooled to −80°C and a solution of methyl benzoate (1.33 g, 9.8 mmol) in anhydrous diethyl ether (10 mL) was gradually added under argon. The resultant mixture was stirred at −80°C for 2 h, allowed to warm to room temperature with stirring, and then poured into water (50 mL). The pH was adjusted to 4–5 by addition of 10% aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer extracted with diethyl ether (2×20 mL). The organic phases were combined and dried (Na_2SO_4). Evaporation of the solvent was followed by flash-chromatography on silica gel (2/1 petroleum ether/diethyl ether). Viscous pale yellow oil; yield 75%; bp 125–126°C/0.1 mmHg. IR (neat, cm^{-1}): 1655 (C═O). ^1H NMR ($CDCl_3$) δ: 2.37 (s, 3H, SCH_3), 7.29 (m, 6H, Ar-*H*), 7.65 (m, 2H, Ar-*H*), 8.15 (m, 1H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 16.76 (SCH_3), 124.32, 127.07, 128.34, 129.74, 130.06, 130.97, 132.96, 137.41,

137.68, 139.06, 196.64 (*C*O). EI-MS *m/z*: 228 (51%, M^+), 213 (100%), 151 (26%), 123 (3%), 105 (19%), 77 (48%), 51 (21%), 45 (26%). Anal calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30; S, 14.04%. Found: C, 73.57; H, 5.35; S, 13.87.

1.1.6. 2-[-(Methylsulfonyl)phenyl](phenyl)methanone (10). To a vigorously stirred solution of **9** (2.3 g, 10 mmol) in dichloromethane (75 mL) 3-chloroperbenzoic acid (4.3 g, 25 mmol)) was gradually added at 5–10°C. After the addition was complete, the reaction mixture was worked up in the same manner described for **5**. The product was flash-chromatographed on silica gel (2/1 petroleum ether/diethyl ether). Yield 78%, crystallized from 1/1 aqueous EtOH as white crystals; mp 128–130°C. IR (nujol, cm^{-1}): 1660 (C═O), 1365 and 1155 (SO_2). ^1H NMR ($CDCl_3$) δ: 3.28 (s, 3H, SC*H*$_3$), 7.71 (m, 9H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 46.19 (S*C*H$_3$), 128.32, 128.53, 129.90, 130.13, 130.45, 132.91, 133.94, 136.27, 139.41, 140.18, 196.28 (*C*O). EI-MS *m/z*: 260 (8%, M^+,), 213 (4%), 183 (22%), 181 (21%), 152 (10%), 105 (100%), 77 (46%), 51 (15%). Anal calcd for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65; S, 12.32%. Found: C, 64.48; H, 4.59; S, 12.15.

1.1.7. 3-Hydroxy-3-phenyl-2,3-dihydro-1*H*-1-benzothiophene-1,1-dioxide (11). A solution of **10** (2 g, 7.7 mmol) in anhydrous terahydrofuran (10 mL) was added dropwise at −80°C into a solution of LDA (7.8 mmol) in anhydrous tetrahydrofuran (10 mL). After the addition was complete, stirring was continued overnight at the same temperature (−80°C). The mixture was then allowed to warm to room temperature with stirring, and then poured into water (50 mL). The pH was adjusted to 4–5 by addition of 10% aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer extracted with diethyl ether (2×20 mL). The organic phases were combined and dried (Na_2SO_4). Evaporation of the solvent was followed by flash-chromatography on silica gel (2/1 petroleum ether/diethyl ether). The crude product was crystallized from 1/1 aqueous EtOH as white crystals. Yield 73%; mp 114–116°C (Lit.[15]). IR (nujol, cm^{-1}): 3450 (OH), 1300 and 1155 (SO_2). ^1H NMR ($CDCl_3$) δ: 3.36 (s. 1H, O*H*, D_2O exchangeable), 3.84 (s, 2H, C*H*$_2$), 7.51 (m, 9H, Ar-*H*). ^{13}C NMR (acetone-d_6) δ: 66.55 (*C*H$_2$), 77.30 (*C*–OH) 120.50, 125.74, 126.74, 128.52, 128.94, 130.65, 134.23, 139.60, 144.31, 145.00. EI-MS *m/z*: 260 (2%, M^+), 242 (31%), 225 (20.5%), 213 (100%), 195 (23%), 194 (25%), 181 (20.5%), 165 (18%), 152 (20.5%), 105 (36%), 91 (32%), 77 (45%), 51 (18%). Anal calcd for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65; S, 12.32%. Found: C, 64.52; H, 4.57; S, 12.20.

1.1.8. 3-Phenyl-1-benzothiophene-1,1-dioxide (12). A solution of **11** (1 g, 3.8 mmol) and *p*-toluenesulfonic (0.1 g) in anhydrous benzene (10 mL) was heated at reflux temperature with stirring for 30 min, then poured into water (50 mL). This mixture was extracted with ether (2×20 mL), washed with water (3×10 mL), dried (Na_2SO_4), and concentrated. Yield 97%; crystallized from EtOH as white crystals; mp 159–160°C (Lit.[17] mp 158–160°C). IR (nujol, cm^{-1}): 1318 and 1155 (SO_2). ^1H NMR ($CDCl_3$) δ: 6.91 (s, 1H, SO_2CH), 7.54 (m, 9H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 121.65, 124.15, 125.78, 128.01, 129.21, 130.62, 131.14, 131.97, 133.28, 138.24, 144.15. EI-MS *m/z*: (%): 242 (M^+, 21.1), 213 (100.0%), 184 (36.0%), 176 (8.0%), 165 (10.9%), 153 (1.7%), 152 (7.8%), 139 (3.9%), 82 (4.3%), 76 (10.2%), 63 (9.6%), 51 (9.6%). Anal calcd for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16; S, 13.23%. Found: C, 69.32; H, 4.21; S, 13.11.

1.1.9. 1-[2-(Methylthio)phenyl]-1-ethanone (13). To a vigorously stirred solution of **8** (2 g, 9.8 mmol) in anhydrous diethyl ether (20 mL) a 1.2 M solution of butyllithium in hexane (7.3 mL, 9.8 mmol) was added dropwise under argon at −25°C and stirring was continued at the same temperature for 0.5 h. The mixture was then cooled to −80°C and a solution of methyl acetate (0.72 g, 9.8 mmol) in anhydrous diethyl ether (10 mL) was gradually added under argon. After the addition was complete, stirring was continued at the same temperature (−80°C) for 2 h. The mixture was then allowed to warm to room temperature with stirring, and then poured into water (50 mL). The pH was adjusted to 4–5 by addition of 10% aqueous hydrochloric acid. The organic layer was separated, and the aqueous layer extracted with diethyl ether (2× 20 mL). The organic phases were combined and dried (Na_2SO_4). Evaporation of the solvent was followed by flash-chromatography on silica gel (2/1 petroleum ether/diethyl ether). Yield 73%; crystallized from 2/1 aqueous EtOH as pale yellow crystals, mp 46–48°C. IR (nujol, cm^{-1}): 1762 (CO). ^1H NMR ($CDCl_3$) δ: 2.31 (s, 3H, SC*H*$_3$), 2.51 (s, 3H, COC*H*$_3$), 7.41 (m, 4H, Ar–*H*). ^{13}C NMR ($CDCl_3$) δ: 16.51 (S*C*H$_3$), 28.82 (CO*C*H$_3$), 124.02, 125.48, 131.81, 133.00, 134.77, 143.34, 199.58 (*C*O). EI-MS *m/z*: 166 (27%, M^+), 151 (100%), 136 (2%), 123 (8%), 108 (7%), 91 (4%), 77 (10%), 69 (7%), 45 (52%), 43 (22%), 39 (4.5%). Anal calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06; S, 19.29%. Found: C, 64.94; H, 5.97; S, 19.16.

1.1.10. 1-[2-(Methylsulfonyl)phenyl]-1-ethanone (14). To a vigorously stirred solution of **13** (1.7 g, 10 mmol) in dichloromethane (75 mL) 3-chloroperbenzoic acid (4.3 g, 25 mmol)) was gradually added at 5–10°C. After the addition was complete, the reaction mixture was worked up in the same manner as described for **12**. The product was flash-chromatographed on silica gel (2/1 petroleum ether/diethyl ether). Yield 76%, crystallized from 1/1 aqueous EtOH as white crystals, mp 97–99°C. IR (nujol, cm^{-1}): 1687 (C═O), 1320 and 1155 (SO_2). ^1H NMR ($CDCl_3$) δ: 2.65 (s, 3H, COC*H*$_3$), 3.25 (s, 3H, SO_2CH_3), 7.68 (m, 4H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 31.01 (CO*C*H$_3$), 46.01 (SO_2*C*H$_3$), 126.29, 129.82, 130.12, 133.48, 137.79, 142.26, 203.35 (*C*O). EI-MS *m/z*: 198 (2%, M^+), 183 (100%), 152 (5%), 141 (3%), 121 (4%), 109 (6.5%), 91 (12%), 77 (15%), 50 (11%), 43 (33%). Anal calcd for $C_9H_{10}O_3S$: C, 54.53; H, 5.08; S, 16.18%. Found: C, 54.61; H, 4.97; S, 16.07.

1.1.11. 3-Hydroxy-3-methyl-2,3-dihydro-1*H*-1-benzothiophene-1,1-dioxide (15). A solution of **14** (2 g, 10.1 mmol) in anhydrous tetrahydrofuran (10 mL) was added dropwise into a solution of LDA (10.2 mmol) in anhydrous tetrahydrofuran (10 mL). After the addition was complete the mixture was worked up in the same manner as described for **11**. The crude product was flash-chromatographed using diethyl ether as eluent. Yield 68%; crystallized as white crystals from 5/1 hexane/acetone, mp 102–104°C (Lit.[15]

mp 105–106°C). IR (nujol, cm^{-1}): 3462 (OH), 1330 and 1150 (SO_2). ^1H NMR ($CDCl_3$) δ: 1.64 (s, 3H, CH_3), 3.06 (s, 1H, O*H*, D_2O exchangeable), 3.46 (s, 2H, CH_2), 7.55 (m, 4H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 28.51 (CH_3), 64.37 (CH_2), 73.52 (*C*OH), 120.88, 124.15, 130.42, 134.33, 137.92, 143.69. EI-MS *m/z*: 198 (M^+, 8%), 183 (100%), 151 (8%), 137 (12%), 119 (12%), 109 (17%), 91 (31%), 77 (20%), 51 (17%), 43 (25%). Anal calcd for $C_9H_{10}O_3S$: C, 54.53; H, 5.08; S, 16.18%. Found: C, 54.42; H, 5.14; S, 16.04.

1.1.12. 3-Methyl-1-benzothiophene-1,1-dioxide (16). A solution of **15** (1 g, 5 mmol), and *p*-toluenesulfonic (0.1 g) in anhydrous benzene (10 mL) was worked up in the same manner as described for **11**. Yield 95%; crystallized from EtOH as white crystals; mp 147–148°C (Lit.[21] mp 145–146°C). ^1H NMR ($CDCl_3$) δ: 2.67 (s, 3H, CH_3), 6.58 (s, 1H, SO_2CH), 7.10 (m, 4H, Ar-*H*). ^{13}C NMR ($CDCl_3$) δ: 13.83 (CH_3), 121.03, 122.46, 125.87, 130.46, 133.10, 134.01, 138.01, 143.05. EI-MS *m/z*: 180 (60.5%, M^+), 151 (100%), 137 (4%), 131 (10%), 119 (3%), 115 (5%), 109 (15%), 91 (29%), 77 (15%), 51 (17%). Anal calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47; S, 17.79%. Found: C, 59.90; H, 4.52; S, 17.64.

Acknowledgements

Financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica, Rome, and by the University of Cagliari (National Project 'Stereoselezione in Sintesi Organica. Metodologie ed Applicazioni') and from the C.N.R. (Italy) is gratefully acknowledged.

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