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Regioselective Synthesis of 3-(Aryloxyacetyl)-2,3-dihydrothieno-[2,3-*b*][1]benzothiopyran-4-ones via Tandem Cyclization

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ABSTRACT

2-[4-Aryloxybut-2-ynylthio][1]benzothiopyran-4-ones on treatment with *m*-chloroperoxy benzoic acid in chloroform at 0°C to room temperature afforded 3-(aryloxyacetyl)-2,3-dihydrothieno[2,3-*b*]benzothiopyrans in 65–70% yield. The sigmatropic [2,3] followed by [3,3] rearrangement, are attributed to this transformation.

Key Words: 2-[4-Aryloxybut-2-ynylthio]benzothiopyran-4-ones; Claisen rearrangement; Heterocycles; Phase-transfer catalysis; Regioselective synthesis; [2,3] Sigmatropic rearrangement.

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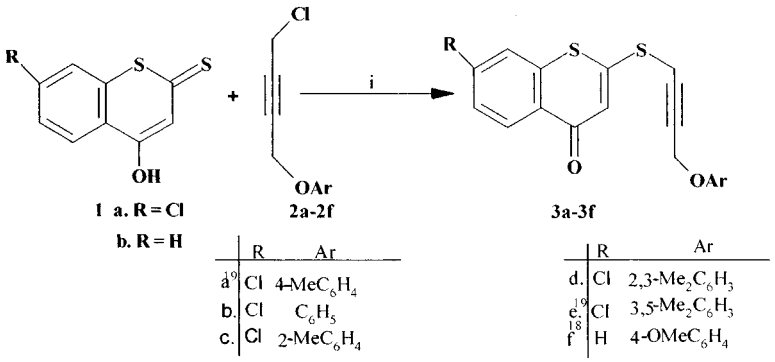
INTRODUCTION

Thieno[2,3-*b*]benzothiopyran-4-one skeleton [1] has been used as an intermediate for the syntheses of a series of anti-psychotic drugs. Literature search revealed that the synthesis [2] of this important intermediate was achieved by a long route. Few years ago, we reported [3] a simple synthesis of thieno-[2,3-*b*]benzothiopyran-4-one and thiopyrano[2,3-*b*]benzothiopyran-5(2*H*)-one skeleton. Construction of the five-membered heterocyclic rings in benzo(*b*)-thiophenes and indoles through the sulphoxide [4–7] and amine oxide [8–10] rearrangements, respectively, was reported by Majumdar and Thyagarajan. Both amine oxide and sulphoxide rearrangement involve the intermediacy of a [2,3] followed by a [3,3] sigmatropic rearrangement. Application of the amine oxide rearrangement [11–13] in heterocyclic substrates [14,15] for the syntheses of a number of tricyclic skeletons has been reported from this laboratory. Recently, we have also reported the regioselective synthesis of thieno[2,3-*f*]-quinolin-7(6*H*)-one and pyrano[3,2-*f*]benzo[*b*]thiophene derivatives [16,17] by the application of the sulphoxide rearrangement. This mild and simple reaction for the construction of the five-membered heterocyclic ring has drawn our interest to undertake a study on the sulphoxide rearrangement of 2-[4-aryloxybut-2-ynylthio][1]benzothiopyran-4-ones (**3a**–**f**). The results are reported here.

RESULTS AND DISCUSSION

The substrates 2-[4-aryloxybut-2-ynylthio][1]benzothiopyran-4-ones (**3a**–**f**) (Sch. 1) were prepared in 80–85% yield according to published procedure.[18]



Scheme 1. Reagents and conditions: (i) NaOH, $CHCl_3$, benzyl triethyl ammonium chloride (BTEAC), r.t, 4 hr.

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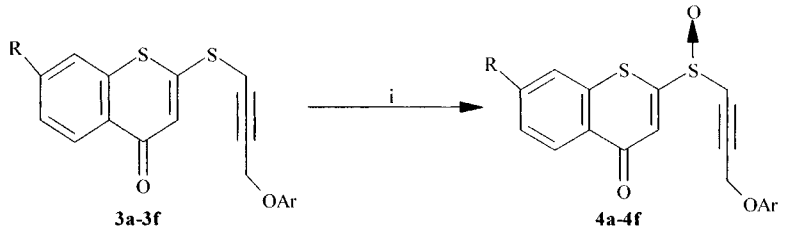
The sulphides **3a–f** were oxidized to the corresponding sulphoxides **4a–f** by the addition of one equivalent of *m*-chloroperoxybenzoic acid (Sch. 2). The reaction was monitored by TLC. Formation of a highly polar sulphoxide was indicated by the appearance of a spot much below (R_f value 0.1 in benzene) that of starting sulphide (R_f value 0.4 in benzene). The sulphoxides **4a–f** are quite unstable. One experiment was carried out in an NMR tube for the characterization of the sulphoxide. After mixing the substrate **3e** with *m*-CPBA in $CDCl_3$ at 0–5°C for 30 min the NMR spectrum was recorded. The spectrum displayed a two proton quartet at δ 3.98 due to the sulphoxido-methylene proton ($^{-}O > S^{+}- C\underline{H}_2$). The $-S-C\mathbf{H}_2-$ in the starting sulphide appears as a triplet at δ 3.83. This clearly indicates the formation of sulphoxide.

The sulphoxides seem to rearrange even during the work up of the reaction mixture. Therefore, these crude sulphides were directly subjected to thermal rearrangement without further purification. The sulphoxide **4a** after removal of chloroform, was refluxed in carbon tetrachloride to give the compound **5a** in 70% yield (Sch. 3).

Compound **5a** was characterized from its elemental analysis and spectral data. The ^{1}H NMR spectrum of **5a** showed three-proton singlet at δ 2.27 due to one $-CH_3$ substituent, two one-proton doublets of a doublet at δ 3.60 ($J = 9.10$, 11.22 Hz) and at 3.68 ($J = 7.20$, 11.22 Hz) due to $-SCH_2$, one proton doublet of a doublet at δ 4.95 ($J = 7.20$, 9.10 Hz) due to one proton of the dihydrothiophene ring, two one-proton doublets at δ 4.90 ($J = 15.10$ Hz) and 5.01 ($J = 15.10$ Hz) due to $-O-CH_2-$, six proton multiplet at δ 6.83–7.58 and one proton doublet at δ 8.37 ($J = 8.51$ Hz). ^{13}C-NMR showed 20 carbons present in the molecule (vide experimental). Mass spectrum of compound **5a** showed a molecular ion peak at m/z 404, 402 (M^+). To test the generality of the reaction five other substrates **4b–f** were subjected to sulphoxide rearrangement under the same reaction condition. All the substrates gave similar products **5b–f** in 65–70% yield.

The formation of the products **5a–f** from the sulphoxides **4a–f** may be explained by the initial [2,3] sigmatropic rearrangement of the sulphoxides



3a-3f **4a-4f**

Scheme 2. Reagents and conditions: (i) *m*-CPBA, $CHCl_3$, 0–5°C, 30 min.

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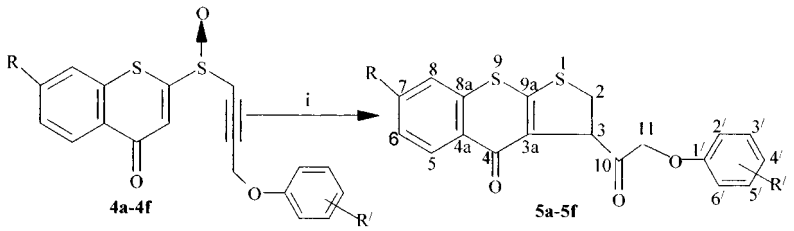
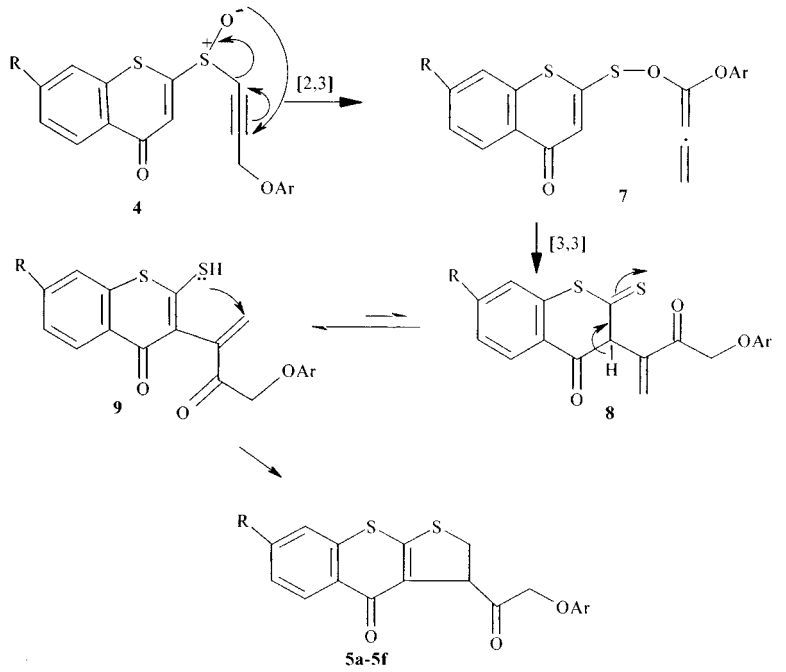


Scheme 3. Reagents and conditions: (i) CCl_4, 4 h.

4 to give the intermediate allenylsulphenates (**7**) followed by a [3,3] sigmatropic rearrangement and enolisation leading to the intermediates **9**, containing an enone moiety favourably juxtaposed to a –SH function for an internal Michael addition of the thiol to the enone moiety to yield **5a–f** (Sch. 4).

The intermediates **9** could have yielded [16,17] **5**. This method is found to be general for the synthesis of 3-(aryloxyacetyl)-2,3-dihydrothieno [2,3-*b*][1]benzothiopyran-4-ones (**5a–f**) in good yield. The reaction is



Scheme 4.

chemoselective. *m*-Chloroperoxybenzoic acid seems to react selectively with only one sulphur leaving the other reactive centre unaffected. The formation of the dihydrothieno[2,3-*b*]benzothiopyran-4-ones system by an intramolecular radical addition has recently been reported by Boivin et al.[19]

EXPERIMENTAL

Melting points were measured on a sulphuric acid bath. UV absorption spectra were recorded on a UV-VIS Spectrophotometer Shimadzu Model No. UV-2401PC (absolute ethanol). IR spectra were run on KBr discs on a Perkin–Elmer 1330 apparatus and FTIR spectrophotometer Perkin–Elmer Model No. L120-000A. ^{1}H-NMR spectra were recorded in $CDCl_3$ with TMS as internal standard on a Bruker DPX-300 (300 MHz) and Bruker DPX-500 (500 MHz) spectrometers. Mass spectra were recorded on a [JEOL D-300 (El)] instrument and elemental analyses (agreeing within the error with calculated values) at RSIC (CDRI) Lucknow. Silica gel (60–120 mesh), Spectrochem, India, was used for chromatographic separation. Petroleum ether refers to the fraction boiling between 60°C and 80°C.

General Procedure for the Alkylation of 7-Chloro-4-hydroxydithiocoumarin

To a mixture of 7-chloro-4-hydroxydithiocoumarin (6 mmol) and 1-aryloxy-4-chlorobut-2-yne (9 mmol) in chloroform (50 mL) is added a solution of TBAB (0.25 mmol) or BTEAC (0.9 mmol) in 1% aq. NaOH (50 mL) and the mixture was stirred at room temperature for a period of 5 hr. The mixture was then diluted with water (100 mL) and extracted with $CHCl_3$ (3 × 25 mL), brine (3 × 25 mL), and dried (Na_2SO_4). The solvent was removed in vacuo and the residual crude mass was purified by chromatography over silica gel using benzene/petroleum ether (1 : 2) as eluent to afford the following compounds.

The sulphides **3a**,[20] **3e**,[20] and **3f**[18] were reported previously.

Compound 3b. Yield (82%); white solid; m.p. 102°C; λ_{max} (nm) 219 ($\log\varepsilon = 4.00$), 271 ($\log\varepsilon = 4.20$), 335 ($\log\varepsilon = 3.85$); $\bar{\nu}_{max}$ (cm^{-1}) 1600, 1580, 1230; δ_H (300 MHz) 3.83 (t, $J = 1.50$ Hz, 2H, SC**H**$_2$), 4.70 (t, $J = 1.50$ Hz, 2H, OC**H**$_2$), 6.84–7.48 (m, 8H, Ar**H**), 8.39 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 374$, 372 (M^+); Anal. calcd for $C_{19}H_{13}ClO_2S_2$: C, 61.29; H, 3.49; Found C, 61.51; H, 3.35%.

Compound 3c. Yield (85%); white solid; m.p. 83°C; λ_{max} (nm) 219 ($\log\varepsilon = 4.02$), 271 ($\log\varepsilon = 4.24$), 336 ($\log\varepsilon = 3.82$); $\bar{\nu}_{max}$ (cm^{-1}) 1600,

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1580, 1280; δ_H (300 MHz) 2.18 (s, 3H, C**H**$_3$), 3.83 (t, $J = 1.50$ Hz, 2H, SC**H**$_2$), 4.72 (t, $J = 1.50$ Hz, 2H, OC**H**$_2$), 6.80–7.48 (m, 7H, Ar**H**), 8.39 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 388$, 386 (M^+); Anal. calcd for $C_{20}H_{15}ClO_2S_2$: C, 62.18; H, 3.89; Found C, 62.26; H, 3.75%.

Compound 3d. Yield (82%); white solid; m.p. 99°C; λ_{max} (nm) 219 ($\log \varepsilon = 4.00$), 271 ($\log \varepsilon = 4.22$), 335 ($\log \varepsilon = 3.81$); $\bar{\nu}_{max}$ (cm^{-1}) 1600, 1580, 1230; δ_H (500 MHz) 2.10 (s, 3H, C**H**$_3$), 2.22 (s, 3H, C**H**$_3$), 3.83 (t, $J = 1.50$ Hz, 2H, SC**H**$_2$), 4.69 (t, $J = 1.50$ Hz, 2H, OC**H**$_2$), 6.72–7.47 (m, 6H, Ar**H**), 8.38 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 402$, 400 (M^+); Anal. calcd for $C_{21}H_{17}ClO_2S_2$: C, 63.00; H, 4.25; Found C, 63.18; H, 4.08%.

General Procedure for the Preparation of Compounds 5a–f

m-Chloroperoxybenzoic acid (50%, 142 mg, 0.41 mmol) in chloroform (20 mL) was slowly added to a well-stirred solution of the sulphide **3a** (150 mg, 0.4 mmol) in chloroform (20 mL) at 0–5°C over a period of 30 min. The reaction mixture was stirred for additional 30 min. Chloroform solution was washed with saturated sodium carbonate solution (3 × 20 mL) followed by water (3 × 20 mL) and dried (Na_2SO_4). The solvent was removed and the residue was refluxed in carbon tetrachloride (25 mL) for 4 hr. Then carbon tetrachloride was removed and a viscous liquid was obtained. It was then chromatographed over silica gel using benzene as eluent to give a solid **5a**, m.p. 150°C; yield 70%.

Compound 5a. Yield (70%); white solid; m.p. 150°C; λ_{max} (nm) 230 ($\log \varepsilon = 4.02$), 270 ($\log \varepsilon = 4.25$), 344 ($\log \varepsilon = 3.80$); $\bar{\nu}_{max}$ (cm^{-1}) 1720, 1600, 1575, 1220; δ_H (300 MHz) 2.27 (s, 3H, C**H**$_3$), 3.60 (dd, $J = 9.10$, 11.22 Hz, 1H, SC**H**$_2$), 3.68 (dd, $J = 7.20$, 11.22 Hz, 1H, SC**H**$_2$), 4.95 (dd, $J = 7.20$, 9.10 Hz, 1H, C**H**), 4.90 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 5.01 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 6.83 (d, $J = 8.40$ Hz, 2H, Ar**H**), 7.07 (d, $J = 15.10$ Hz, 2H, Ar**H**), 7.45–7.58 (m, 2H, Ar**H**), 8.37 (d, $J = 8.51$ Hz, 1H, Ar**H**); δ_C (75.5 MHz) 20.45 (4′CH_3), 35.37 (C_2), 65.01 (C_3), 73.00 (C_{11}), 114.46 ($C_{2'}$), 114.59 ($C_{6'}$), 125.00 (C_{9a}), 125.195 (C_8), 127.56 (C_6), 128.45 (C_5), 128.83 ($C_{4'}$), 130.07 ($C_{3'}$), 130.18 ($C_{5'}$), 130.96 (C_{4a}), 131.04 (C_7), 137.50 (C_{8a}), 138.02 (C_{3a}), 155.65 ($C_{1'}$), 174.50 (C_{10}), 204.87 (C_4); $m/z = 404$, 402 (M^+); Anal. calcd for $C_{20}H_{15}ClO_3S_2$: C, 59.70; H, 3.73; Found C, 58.91; H, 3.58%.

Compound 5b. Yield (70%); white solid; m.p. 180°C; λ_{max} (nm) 220 ($\log \varepsilon = 4.00$), 272 ($\log \varepsilon = 4.21$), 340 ($\log \varepsilon = 3.75$); $\bar{\nu}_{max}$ (cm^{-1}) 1720, 1600, 1575, 1220; δ_H (300 MHz) 3.62 (dd, $J = 9.10$, 11.22 Hz, 1H, SC**H**$_2$), 3.70 (dd, $J = 7.20$, 11.22 Hz, 1H, SC**H**$_2$), 4.95 (dd, $J = 7.20$, 9.10 Hz, 1H, C**H**), 4.91 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 5.02 (d, $J = 15.20$ Hz,

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1H, OC**H**$_2$), 6.93–7.53 (m, 7H, Ar**H**), 8.39 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 390$, 388 (M^+); Anal. calcd for $C_{19}H_{13}ClO_3S_2$: C, 58.76; H, 3.35; Found C, 58.57; H, 3.52%.

Compound 5c. Yield (67%); white solid; m.p. 138°C; λ_{max} (nm) 223 ($\log \varepsilon = 3.61$), 230 ($\log \varepsilon = 3.74$), 269 ($\log \varepsilon = 3.93$); $\bar{\nu}_{max}$ (cm^{-1}) 1710, 1580, 1560, 1220; δ_H (500 MHz) 2.29 (s, 3H, C**H**$_3$), 3.63 (dd, $J = 9.10$, 11.22 Hz, 1H, SC**H**$_2$), 3.70 (dd, $J = 7.20$, 11.22 Hz, 1H, SC**H**$_2$), 5.01 (dd, $J = 7.20$, 9.10 Hz, 1H, C**H**), 4.87 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 5.02 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 6.76–7.53 (m, 6H, Ar**H**), 8.38 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 404$, 402 (M^+); Anal. calcd for $C_{20}H_{15}ClO_3S_2$: C, 59.70; H, 3.73; Found C, 59.62; H, 3.58%.

Compound 5d. Yield (65%); white solid; m.p. 120°C; λ_{max} (nm) 220 ($\log \varepsilon = 3.59$), 270 ($\log \varepsilon = 3.75$), 340 ($\log \varepsilon = 3.84$); $\bar{\nu}_{max}$ (cm^{-1}) 1710, 1580, 1560, 1220; δ_H (300 MHz) 2.17 (s, 3H, C**H**$_3$), 2.27 (s, 3H, C**H**$_3$), 3.62 (dd, $J = 9.10$, 11.22 Hz, 1H, SC**H**$_2$), 3.69 (dd, $J = 7.20$, 11.22 Hz, 1H, SC**H**$_2$), 5.01 (dd, $J = 7.20$, 9.10 Hz, 1H, C**H**), 4.85 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 5.00 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 6.63–7.53 (m, 6H, Ar**H**), 8.38 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 418$, 416 (M^+); Anal. calcd for $C_{21}H_{17}ClO_3S_2$: C, 60.58; H, 4.09; Found C, 60.49; H, 4.25%.

Compound 5e. Yield (68%); white solid; m.p. 161°C; λ_{max} (nm) 220 ($\log \varepsilon = 3.51$), 272 ($\log \varepsilon = 3.67$), 336 ($\log \varepsilon = 3.81$); $\bar{\nu}_{max}$ (cm^{-1}) 1710, 1600, 1570, 1280; δ_H (300 MHz) 2.17 (s, 3H, C**H**$_3$), 2.23 (s, 3H, C**H**$_3$), 3.60 (dd, $J = 9.10$, 11.22 Hz, 1H, SC**H**$_2$), 3.67 (dd, $J = 7.20$, 11.22 Hz, 1H, SC**H**$_2$), 4.99 (dd, $J = 7.20$, 9.10 Hz, 1H, C**H**), 4.88 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 5.06 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 6.55–7.52 (m, 6H, Ar**H**), 8.38 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 418$, 416 (M^+); Anal. calcd for $C_{21}H_{17}ClO_3S_2$: C, 60.58; H, 4.09; Found C, 60.43; H, 4.23%.

Compound 5f. Yield (70%); white solid; m.p. 130°C; λ_{max} (nm) 233 ($\log \varepsilon = 4.33$), 267 ($\log \varepsilon = 4.34$), 342 ($\log \varepsilon = 4.06$); $\bar{\nu}_{max}$ (cm^{-1}) 1720, 1590, 1570, 1210; δ_H (300 MHz) 3.61 (dd, $J = 9.10$, 11.22 Hz, 1H, SC**H**$_2$), 3.69 (dd, $J = 7.20$, 11.22 Hz, 1H, SC**H**$_2$), 3.73 (s, 3H OC**H**$_3$), 5.01 (dd, $J = 7.20$, 9.10 Hz, 1H, C**H**), 4.88 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 4.95 (d, $J = 15.20$ Hz, 1H, OC**H**$_2$), 6.80–7.58 (m, 7H, Ar**H**), 8.47 (d, $J = 8.51$ Hz, 1H, Ar**H**); $m/z = 420$, 418 (M^+); Anal. calcd for $C_{21}H_{17}ClO_3S_2$: C, 57.42; H, 3.83; Found C, 57.83; H, 3.91%.

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