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Regioselective synthesis of indole-annulated sulfur heterocycles by tri-*n*-butyltin hydride-mediated aryl radical cyclization

K. C. Majumdar[a]; P. Debnath[a]; S. Alam[a]; R. Islam[a]
[a] Department of Chemistry, University of Kalyani, Kolkata, West Bengal, India

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Regioselective synthesis of indole-annulated sulfur heterocycles by tri-*n*-butyltin hydride-mediated aryl radical cyclization

K.C. Majumdar*, P. Debnath, S. Alam and R. Islam

Department of Chemistry, University of Kalyani, Kolkata, West Bengal, India

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2-[(2-Bromobenzyl)sulfonyl]indoles under Bu_3SnH-mediated aryl radical cyclization furnished exclusively the benzo[c]thiopyrano[2,3-*b*]indoles in 56–61% yields via 6-*endo-trig* cyclization whereas 2-[(2-bromobenzyl)sulfanyl]indole **3a** gave only the β-scission product.

Keywords: indole; Bu_3SnH–AIBN; aryl radical cyclization; sulfur heterocycles; 6-*endo-trig*

1. Introduction

Recently, free radical-mediated cyclization has been developed as a potential method for the construction of carbon–carbon bonds in synthetic organic chemistry (*1*, *2*). In particular, the synthesis of sulfur heterocycles by radical pathway presents a major challenge in organic synthesis. A few examples of radical cyclization reactions involving the synthesis of sulfur heterocycles have been reported (*3*). Flanagan and Harrowven (*4*) described a series of radical cyclization reactions in which an indole is employed as a radical acceptor. However, there is no report on the radical cyclization containing sulfur heterocycles. We have successfully synthesized quinolone and coumarinannulated [6, 6] fused sulfur heterocycles (*3a*,*b*) by Bu_3SnH-mediated radical cyclization where a small amount of β-scission (*5*) product was formed along with 6-*endo* cyclization. However, when a highly electron-withdrawing SO_2 group is attached to the radical center, it confers considerable stability (lower energy of the singly occupied molecular orbital [SOMO]) to the intermediate radical and prevents the β-scission with an increase in the product yield.

Synthesis of substituted indole derivatives has been a topic of great interest for many years because the indole moiety is a key structural feature found in numerous natural products, many of these compounds exhibit potent pharmacological activity (*6*). Indole or an indole-related nucleus possessing a side chain or another heterocycle containing one or two sulfur atoms is present in several cruciferous phytoalexins, such as brassinin, methoxybrassinin, cyclobrassinin, and spirobrassinin (*7*). Many of these compounds exhibit a vast array of bioactivity viz antimicrobial (*8*), antitumor (*9*), and oviposition stimulant (*10*) activities. Some tetrahydrothiopyrano[2,3-b]indole

*Corresponding author. Email: kcm_ku@yahoo.co.in

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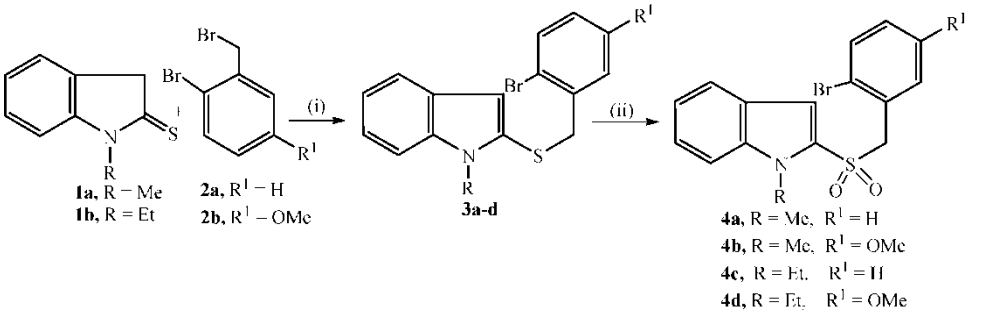
derivatives are known to possess analgesic activity (*11*). The tetrahydrothiopyrano[3,2-*b*]indole derivatives and their pharmaceutically acceptable salts are also useful as psychoanaleptic and nootropic drugs (*12*). This prompted us to undertake a study of the radical cyclization of 2-[(2-bromobenzyl)sulfanyl]indole and 2-[(2-bromobenzyl)sulfonyl]indoles in order to achieve the synthesis of indole-annulated sulfur heterocycles. Herein we report the results of our investigation.

2. Results and discussion

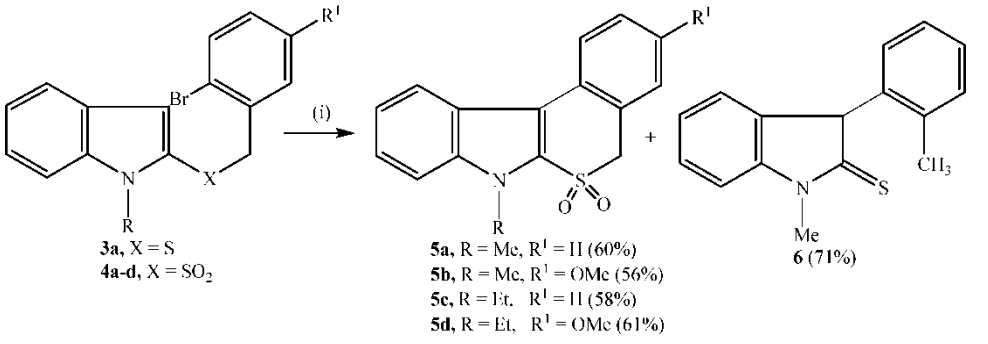
Required precursors for our present study, 2-[(2-bromobenzyl)sulfanyl]indoles (**3a–d**), were prepared in 85–93% yields by the phase transfer catalyzed reaction of different indoline-2-thiones (**1a, b**) with 2-bromobenzyl bromides (**2a, b**) in dichloromethane and 1% NaOH solution in the presence of benzyltriethylammonium chloride (BTEAC) at room temperature. The corresponding sulfones **4a–d** were synthesized in 77–90% yields by the oxidation of **3a–d** with *m*-CPBA (2.5 equiv.) in dichloromethane at 40 °C for 2 h (Scheme 1). Compounds **3a–d** and **4a–d** were characterized from their elemental analyses and spectroscopic data.



Scheme 1. Reagents and conditions: (i) BTEAC, 1% aq. NaOH, CH_2Cl_2, rt, 15 min. (ii) *m*-CPBA, CH_2Cl_2, 40 °C, 2 h.

Compound **3a** was dissolved in dry degassed toluene along with Bu_3SnH (1.1 equiv.) and AIBN (0.5 equiv.) and was heated at 80 °C for 1 h. A single product, solid, mp: 92–94 °C was isolated by column chromatography. The ^1H NMR spectra of the product revealed that no cyclization product was formed. Compound **3a** afforded the β-scission product **6** under cyclization conditions. We then tried to carry out the cyclization reaction in the presence of Bu_3SnCl, $Na(CN)BH_3$ instead of Bu_3SnH. We also examined the reaction by changing the concentration of the tin-reagent, reaction temperature, solvent, and reaction time. But we failed to achieve the radical cyclization. However, β-scission product was eliminated by conversion of the sulfides to the sulfones. The conditions for the Bu_3SnH–AIBN procedure were optimized for the six-membered radical cyclization of 2-[(2-bromobenzyl)sulfonyl]indoles. Substrate **4a** was refluxed in degassed dry toluene under nitrogen atmosphere with excess of AIBN (2.5 equiv.) (*13*) and Bu_3SnH (1.2 equiv.) for 18 h (Scheme 2). Isolation of the product by flash chromatography furnished a solid **5a**, mp: 142–144 °C in 60% yield. The product was characterized as the benzo[c]thiopyrano[2,3-*b*]indole derivative on the basis of its spectral and analytical data. Encouraged by this result, substrates **4b–d** were similarly treated to give **5b–d** in 56–61% yields.

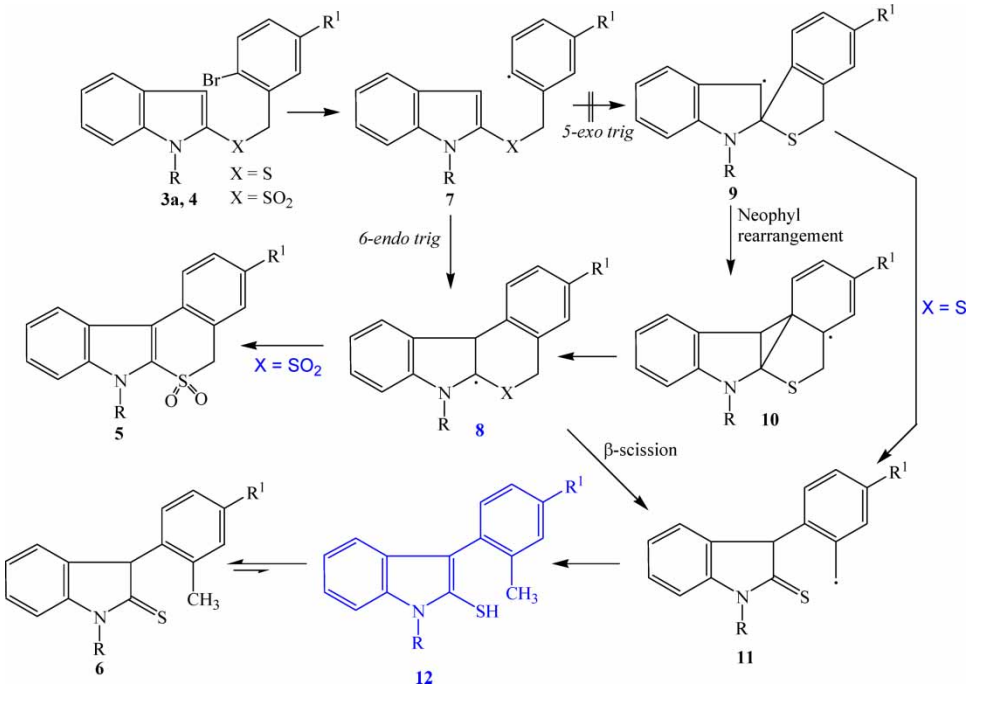
The formation of products **5** and β-scission product **6** may be explained by the generation of an aryl radical **7**. The aryl radical **7** may undergo either a 6-*endo trig* or a 5-*exo trig* cyclization at the double bond of the pyrrole ring of the indole moiety. A 6-*endo trig* cyclization of radical **7** may



Scheme 2. Reagents and conditions: (i) Bu_3SnH (1.2 equiv.), AIBN (2.5 equiv.), dry toluene, N_2 atms., reflux, 18–20 h for **4a–d**, Bu_3SnH (1.1 equiv.), AIBN (0.5 equiv.), dry toluene, N_2 atms., 80 °C, 1 h for **3a**.

produce the intermediate radical **8**, while 5-*exo trig* cyclization may give the spiroheterocyclic radical **9**, followed by neophyl rearrangement (*14*) to radical intermediate **8**. Oxidative elimination of hydrogen from **8** may afford **5** (Scheme 3).

In case of compounds **4**, the 5-*exo trig* cyclization to give spiroheterocyclic radical **9** followed by a neophyl rearrangement is highly unlikely in the present instance. It is known that β-fragmentation of alkylthiyl radicals is very fast (*15*) (10^8 s^{-1}) when compared with neophyl-type rearrangements, which are much slower (*16*) (about 10^3–10^4 s^{-1}). Therefore, neophyl rearrangement of radical **9** could not compete with the β-fragmentation reaction. β-Fragmentation leads to β-scission product **6** from **3a** (X = S) via radical intermediate **11**. Although thioenol **12** is expected to be the final product after β-fragmentation of **3a** from Bu_3SnH-mediated reaction, we were unable to detect any absorption signal for –SH in the IR spectrum perhaps due to conversion of thioenol



Scheme 3.

12 into its stable tautomer **6** during the workup procedure. In case of compounds **4**, the other reason for the formation of six-membered product may be due to the presence of highly electron withdrawing SO_2 group attached to the radical center which confers considerable electrophilic character onto the radical and favors the formation of the 6-*endo* products.

In conclusion, we have successfully performed the Bu_3SnH-mediated aryl radical cyclization for the synthesis of less studied sulfur containing six-membered heterocyclic compounds. The methodology described here is mild and shows appreciable regioselectivity.

3. Experimental

Melting points were determined in an open capillary and are uncorrected. IR spectra were recorded on a Perkin–Elmer L 120-000A spectrometer (ν_{max} in cm^{-1}) on KBr disks. ^1H NMR (400 MHz, 500 MHz) and ^{13}C NMR (125.0 MHz) spectra were recorded on a Varian-400 FT-NMR and Bruker DPX-500 spectrometers in $CDCl_3$ (chemical shifts in δ) with tetramethylsilane (TMS) as internal standard. Silica gel [(60–120 mesh), Spectrochem, India] was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for thin layer chromatography (TLC). Petroleum ether refers to the fraction boiling between 60 and 80 °C.

3.1. *Preparation of 2-[(2-bromobenzyl)sulfanyl]indoles (3a–d)*

3.1.1. *General procedure*

To a mixture of 1-methylindoline-2-thione 1a or 1-ethylindoline-2-thione **1b** (3 mmol) and 2-bromobenzylbromides **2a, b** (3 mmol) in dichloromethane (30 mL) was added a solution of benzyltriethylammonium chloride (BTEAC, 0.5 g, 1.8 mmol) in 1% aqueous NaOH (30 mL) and the mixture was magnetically stirred at rt for 15 min. The reaction mixture was then diluted with water (20 mL) and the dichloromethane layer was washed with 2N HCl (2 × 20 mL), water (2 × 20 mL), brine (20 mL), and dried (Na_2SO_4). Removal of dichloromethane left a oily residue, which was subjected to column chromatography over silica gel (230–400 mesh). Elution of the column with petroleum ether–ethyl acetate (49:1) afforded compounds **3a–d**.

3.2. *Data*

3.2.1. *2-[(2-Bromobenzyl)sulfanyl]-1-methyl-1H-indole (3a)*

Yield 91%; solid; mp: 76–78 °C (benzene–hexane); IR (neat): $\nu_{max} = 2928, 1322, 1080\,cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 3.49$ (s, 3H, $-NCH_3$), 4.03 (s, 2H, $-SCH_2$), 6.68 (s, 1H, =CH), 6.82 (dd, $J = 1.6, 7.2$ Hz, 1H, ArH), 7.02–7.22 (m, 5H, ArH), 7.54 (d, $J = 7.7$ Hz, 2H, ArH); MS: $m/z = 331, 333$ (M^+). Anal. Calcd. for $C_{16}H_{14}BrNS$: C, 57.84; H, 4.25; N, 4.22%. Found: C, 57.98; H, 4.32; N, 4.31%.

3.2.2. *2-[(2-Bromo-5-methoxybenzyl)sulfanyl]-1-methyl-1H-indole (3b)*

Yield: 88%; solid; mp: 65–67 °C (benzene–hexane); IR (neat): $\nu_{max} = 2932, 1310, 1011\,cm^{-1}$; ^1H NMR (400 MHz, CDCl3): $\delta_H = 3.29$ (s, 3H, $-OCH_3$), 3.47 (s, 3H, $-NCH_3$), 3.97 (s, 2H, $-SCH_2$), 6.23 (d, $J = 3.2$ Hz, 1H, ArH), 6.62 (dd, $J = 3.2, 8.8$ Hz, 1H, ArH), 6.72 (s, 1H, =CH), 7.07–7.21 (m, 3H, ArH), 7.39 (d, $J = 8.8$ Hz, 1H, ArH), 7.54 (d, $J = 7.6$ Hz, 1H, ArH); MS:

m/z = 361, 363 (M^+). Anal. Calcd. for $C_{17}H_{16}BrNOS$: C, 56.36; H, 4.45; N, 3.87%. Found: C, 56.55; H, 4.41; N, 3.93%.

3.2.3. *2-[(2-Bromobenzyl)sulfanyl]-1-ethyl-1H-indole (3c)*

Yield: 93%; solid; mp: 87–89 °C (benzene–hexane); IR (neat): ν_{max} = 2929, 1333, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 1.23 (t, J = 7.2 Hz, 3H, $-NCH_2CH_3$), 4.08 (s, 2H, $-SCH_2$), 4.11 (q, J = 7.2 Hz, 2H, $-NCH_2CH_3$), 6.61 (s, 1H, =CH), 6.93 (dd, J = 3.2, 7.4 Hz, 1H, ArH), 7.05–7.34 (m, 6H, ArH), 7.51–7.58 (m, 1H, ArH); MS: m/z = 345, 347 (M^+). Anal. Calcd. for $C_{17}H_{16}BrNS$: C, 58.96; H, 4.66; N, 4.04%. Found: C, 59.07; H, 4.83; N, 3.96%.

3.2.4. *2-[(2-Bromo-5-methoxybenzyl)sulfanyl]-1-ethyl-1H-indole (3d)*

Yield: 85%; gummy mass; IR (neat): ν_{max} = 2924, 1290, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 1.22 (t, J = 7.2 Hz, 3H, $-NCH_2CH_3$), 3.38 (s, 3H, OCH_3), 4.02 (s, 2H, $-SCH_2$), 4.06 (q, J = 7.1 Hz, 2H, $-NCH_2CH_3$), 6.36 (d, J = 2.7 Hz, 1H, ArH), 6.63 (d, J = 2.8 Hz, 1H, ArH), 6.66 (s, 1H, =CH), 7.05 (t, J = 7.2 Hz, 1H, ArH), 7.17–7.32 (m, 2H, ArH), 7.40 (d, J = 8.7 Hz, 1H, ArH), 7.53 (d, J = 7.8 Hz, 1H, ArH); MS: m/z = 375, 377 (M^+). Anal. Calcd. for $C_{18}H_{18}BrNOS$: C, 57.45; H, 4.82; N, 3.72%. Found: C, 57.54; H, 4.85; N, 3.77%.

3.3. *Preparation of 2-[(2-bromobenzyl)sulfonyl]indoles (4a–d)*

3.3.1. *General procedure*

To a stirred solution of compound 2-[(2-bromobenzyl)sulfanyl]indoles **3a–d** (1.5 mmol) in CH_2Cl_2 (15 ml), a solution of *m*-CPBA (77%, 840 mg, 4.86 mmol, 2.5 equiv.) in CH_2Cl_2 (10 mL) was added over a period of 0.5 h. After complete addition of *m*-CPBA, the reaction was refluxed for another 2 h for complete conversion (TLC). The reaction mixture was then cooled and washed with saturated solution of sodium carbonate (3 × 10 mL), brine (10 mL), and dried (Na_2SO_4). The solvent was removed and the crude mass obtained was purified by column chromatography over silica gel using 20% ethyl acetate in petroleum ether as eluant to afford 2-[(2-bromobenzyl)sulfonyl]indoles **4a–d**.

3.4. *Data*

3.4.1. *2-[(2-Bromobenzyl)sulfonyl]-1-methyl-1H-indole (4a)*

Yield: 80%; solid; mp: 132–134 °C (acetonitrile–methanol); IR (neat): ν_{max} = 2924, 1310, 1124 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 3.64 (s, 3H, $-NCH_3$), 4.71 (s, 2H, $-SO_2CH_2$), 7.10 (s, 1H, =CH), 7.17–7.21 (m, 2H, ArH), 7.26–7.46 (m, 5H, ArH), 7.63 (d, J = 8.1 Hz, 1H, ArH); MS: m/z = 363, 365 (M^+). Anal. Calcd. for $C_{16}H_{14}BrNO_2S$: C, 52.76; H, 3.87; N, 3.85%. Found: C, 52.99; H, 3.94; N, 3.89%.

3.4.2. *2-[(2-Bromo-5-methoxybenzyl)sulfonyl]-1-methyl-1H-indole (4b)*

Yield: 77%; solid; mp: 118–120 °C (acetonitrile–methanol); IR (neat): ν_{max} = 2915, 1319, 1130 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 3.58 (s, 3H, $-OCH_3$), 3.65 (s, 3H, $-NCH_3$), 4.64 (s, 2H, $-SO_2CH_2$), 6.74–6.78 (m, 2H, ArH), 7.14 (s, 1H, =CH), 7.16 (t, J = 7.4 Hz, 1H,

ArH), 7.30–7.42 (m, 3H, ArH), 7.64 (d, $J = 8.0$ Hz, 1H, ArH); MS: $m/z = 393, 395$ (M^+). Anal. Calcd. for $C_{17}H_{16}BrNO_3S$: C, 51.79; H, 4.09; N, 3.55%. Found: C, 51.69; H, 4.14; N, 3.67%.

3.4.3. *2-[(2-Bromobenzyl)sulfonyl]-1-ethyl-1H-indole (4c)*

Yield: 84%; gummy mass; IR (neat): $\nu_{max} = 2924, 1324, 1129\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 1.34$ (t, $J = 7.0$ Hz, 3H, $-NCH_2CH_3$), 4.13 (q, $J = 7.0$ Hz, 2H, $-NCH_2CH_3$), 4.68 (s, 2H, $-SO_2CH_2$), 7.06 (s, 1H, =CH), 7.16–7.21 (m, 2H, ArH), 7.27 (dd, $J = 1.0, 7.2$ Hz, 1H, ArH), 7.30–7.41 (m, 3H, ArH), 7.45 (dd, $J = 1.1, 8.0$ Hz, 1H, ArH), 7.64 (d, $J = 8.0$ Hz, 1H, ArH); MS: $m/z = 377, 379$ (M^+). Anal. Calcd. for $C_{17}H_{16}BrNO_2S$: C, 53.98; H, 4.26; N, 3.70%. Found: C, 54.26; H, 4.20; N, 3.77%.

3.4.4. *2-[(2-Bromo-5-methoxybenzyl)sulfonyl]-1-ethyl-1H-indole (4d)*

Yield: 90%; solid; mp: 98–100 °C (acetonitrile–methanol); IR (neat): $\nu_{max} = 2916, 1316, 1131\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 1.33$ (t, $J = 7.1$ Hz, 3H, $-NCH_2CH_3$), 3.47 (s, 3H, $-OCH_3$), 4.15 (q, $J = 7.0$ Hz, 2H, $-NCH_2CH_3$), 4.63 (s, 2H, $-SO_2CH_2$), 6.73–6.76 (m, 2H, ArH), 7.07 (s, 1H, =CH), 7.16 (t, $J = 7.2$ Hz, 1H, ArH), 7.32–7.41 (m, 3H, ArH), 7.64 (d, $J = 8.0$ Hz, 1H, ArH); MS: $m/z = 407, 409$ (M^+). Anal. Calcd. for $C_{18}H_{18}BrNO_3S$: C, 52.95; H, 4.44; N, 3.43%. Found: C, 52.89; H, 4.47; N, 3.51%.

3.5. *Radical reaction of the compounds 3a and (4a–d)*

3.5.1. *General procedure*

Bu_3SnH (0.18 mL, 0.66 mmol) was added dropwise under nitrogen atmosphere to a magnetically stirred solution of **4a–d** (0.55 mmol) and azobis(isobutyro)nitrile (225 mg, 1.37 mmol) in dry degassed toluene (10 mL). The mixture was refluxed for 18–20 h. After the completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (15 mL) and stirred with 10% aqueous KF solution (10 mL) for 1 h. The aqueous phase was extracted with CH_2Cl_2 (3×15 mL). The combined CH_2Cl_2 extract was washed with water (2×20 mL), brine solution (1×20 mL), and dried (Na_2SO_4). The solvent was removed and the residual mass was subjected to column chromatography over silica gel using petroleum ether:ethyl acetate (4:1) as eluant to give **5a–d**. Similar treatment of compound **3a** with Bu_3SnH (1.1 equiv.) and AIBN (0.5 equiv.) and similar workup procedure as stated above gave only the β-scission product **6**.

3.6. *Data*

3.6.1. *7-Methyl-6,7-dihydro-5H-6λ⁶-isothiochromeno[3,4-b]indole-6,6-dione (5a)*

Yield: 60%; solid; mp: 142–144 °C (benzene–hexane); IR (neat): $\nu_{max} = 2923, 1318, 1124\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta_H = 3.32$ (s, 3H, $-NCH_3$), 4.43 (s, 2H, $-SO_2CH_2$), 7.03 (d, $J = 7.3$ Hz, 1H, ArH), 7.19 (d, $J = 7.5$ Hz, 1H, ArH), 7.22–7.24 (m, 3H, ArH). 7.33–7.40 (m, 2H, ArH), 7.68 (d, $J = 8.0$ Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta_c = 31.2, 63.4, 113.1, 121.6, 123.2, 123.3, 125.6, 126.2, 126.4, 128.1, 128.4, 129.1, 130.9, 131.3, 133.5, 133.6$; MS: $m/z = 283$ (M^+). Anal. Calcd. for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 4.94%. Found: C, 68.03; H, 4.69; N, 4.98%.

3.6.2. *3-Methoxy-7-methyl-6,7-dihydro-5H-6λ^6-isothiochromeno[3,4-b]indole-6,6-dione (5b)*

Yield: 56%; solid; mp: 122–123 °C (benzene–hexane); IR (neat): $\nu_{max} = 2915, 1319, 1130\,cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta_H = 3.36$ (s, 3H, $-NCH_3$), 3.46 (s, 3H, $-OCH_3$), 4.40 (s, 2H, $-SO_2CH_2$), 6.43 (s, 1H, ArH), 6.63 (d, $J = 6.5$ Hz, 1H, ArH), 6.87 (d, $J = 6.5$ Hz, 1H, ArH), 7.13–7.21 (m, 2H, ArH), 7.37–7.39 (m, 1H, ArH), 7.68 (d, $J = 7.5$ Hz, 1H, ArH); MS: $m/z = 313$ (M^+). Anal. Calcd. for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.82; N, 4.47%. Found: C, 65.25; H, 4.77; N, 4.58%.

3.6.3. *7-Ethyl-6,7-dihydro-5H-6λ^6-isothiochromeno[3,4-b]indole-6,6-dione (5c)*

Yield: 58%; solid; mp: 105–107 °C (benzene–hexane); IR (neat): $\nu_{max} = 2921, 1310, 1119\,cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 1.54$ (t, $J = 7.1$ Hz, 3H, $-NCH_2CH_3$), 4.16 (s, 2H, $-SO_2CH_2$), 4.61 (q, $J = 7.3$ Hz, 2H, $-NCH_2CH_3$), 7.28–7.37 (m, 3H, ArH), 7.43–7.52 (m, 3H, ArH), 8.06 (d, $J = 7.4$ Hz, 1H, ArH), 8.15 (d, $J = 8.0$ Hz, 1H, ArH); MS: $m/z = 297$ (M^+). Anal. Calcd. for $C_17H_15NO_2S$: C, 68.66; H, 5.08; N, 4.71%. Found: C, 68.78; H, 5.06; N, 4.77%.

3.6.4. *7-Ethyl-3-methoxy-6,7-dihydro-5H-6λ^6-isothiochromeno[3,4-b]indole-6,6-dione (5d)*

Yield: 61%; solid; mp: 99–101 °C (benzene–hexane); IR (neat): $\nu_{max} = 2912, 1319, 1133\,cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 1.33$ (t, $J = 7.0$ Hz, 3H, $-NCH_2CH_3$), 3.56 (s, 3H, $-OCH_3$), 4.16 (s, 2H, $-SO_2CH_2$), 4.63 (q, $J = 6.7$ Hz, 2H, $-NCH_2CH_3$), 6.73 (d, $J = 7.6$ Hz, 1H, ArH), 7.12–7.39 (m, 5H, ArH), 7.64 (d, $J = 8.2$ Hz, 1H, ArH); MS: $m/z = 327$ (M^+). Anal. Calcd. for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.28%. Found: C, 66.16; H, 5.41; N, 4.36%.

3.6.5. *1-Methyl-3-(2-methylphenyl)-2-indolinethione (6)*

Yield: 71%; solid; mp: 92–94 °C (hexane only); IR (neat): $\nu_{max} = 2954, 1336, 1128\,cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 2.19$ (s, 3H, $ArCH_3$), 3.51 (s, 3H, $-NCH_3$), 6.43 (s, 1H, $-CH$), 7.12 (t, $J = 7.3$ Hz, 1H, ArH), 7.22–7.36 (m, 6H, ArH), 7.63 (d, $J = 7.7$ Hz, 1H, ArH); MS: $m/z = 253$ (M^+). Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53%. Found: C, 75.78; H, 6.02; N, 5.56%.

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