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Regioselective synthesis of functionalized naphtho[*b*]thiophenes through a 'lactone methodology'☆

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Abstract—Benzo[*b*]thiophene and its benzannulated derivatives are important classes of compounds due to their unique chemical properties and biosteric relationship with indole. In this letter, we report a convenient route for the synthesis of substituted naphtho[*b*]thiophenes through a ring transformation reaction of suitably functionalized 2*H*-pyran-2-ones with 6,7-dihydro-5*H*-benzothiophene-4-one, in good yields.

The chemical and biological potentials of five-membered heterocyclic compounds fused with aromatic nuclei have attracted the attention of organic and medicinal chemists for several years. Amongst these, indole and benzofuran and their annulated derivatives have been extensively explored, since compounds containing these scaffolds demonstrate diverse and interesting biological activities. A survey of the literature on these ring systems revealed a paucity of references to benzo[*b*]thiophenes and naphtho[*b*]thiophenes. A few synthetic approaches are available in the literature for the synthesis of benzo[*b*]thiophenes,[1] however, there are fewer approaches to naphtho[*b*]thiophenes.[2–4] Some interesting biological activities such as antifungal,[5] anti-plasmodial,[6] anti-trypansomal[6] and antimalarial activities[7] associated with the naphtho[*b*]thiophene ring system are reported in the literature.

Naphtho[*b*]thiophenes are generally synthesized either by the fabrication of a thiophene ring onto a mercaptonaphthol precursor[2,3] or by photocyclization/photooxidation[4] of 3-styrylthiophene substrates. The former approach affords mainly 1,2-substituted naphtho[*b*]thiophenes, which offers two point diversity in their molecular architecture. The application of this procedure limits the scope of derivatization on the aromatic ring simply because of the poor availability of functionalized thionaphthols. The latter photocyclization method is extremely dependent on geometrical isomerism of the substrate and the reaction conditions employed and suffers from low yields of the desired compounds due to the formation of undesired by-products. Junjappa et al.[8] developed an efficient regiocontrolled synthesis of various polycyclic benzo[*b*]thiophenes through their benzoannulation strategy. Recently, benzothiophenes and a naphthothiophene were prepared via a multi-step procedure involving a directed metalation strategy.[9] The paucity of synthetic methods for preparing naphtho[*b*]thiophenes and the limitations of existing procedures prompted us to develop an efficient synthetic route, which could offer the flexibility of introducing electron donor or acceptor substituents on the aromatic ring.

During studies on the chemistry of 2*H*-pyran-2-ones, we discovered for the first time, an elegant route for the synthesis of 1,3-terphenyls through a carbanion-induced ring transformation reaction of 2*H*-pyran-2-ones and acetophenones under basic conditions at room temperature.[10] This novel conversion of an α-pyranone ring to a benzene ring (termed as 'Lactone Methodology') utilizing methylenecarbonyl compounds under mild basic conditions encouraged us to explore this methodology for preparing various arenes and heteroarenes of particular importance.[11] The unique feature of 2*H*-pyran-2-ones **1** is the presence of three electrophilic centres; C2, C4 and C6, which can be exploited regioselectively

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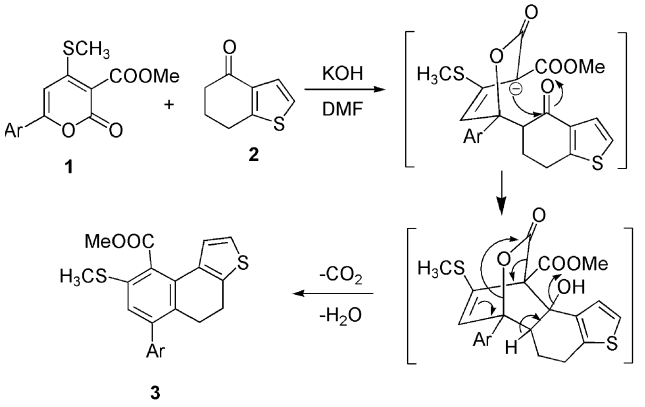
by reacting with various C-, N- and S-nucleophiles to generate molecular diversity. Recently, we regioselectively synthesized functionalized biaryls through our lactone methodology using malononitrile or acetyltrimethylsilane as a carbanion source.[12] Herein, we report an elegant route for preparing functionalized naphtho[*b*]thiophenes, using our developed chemistry on 2*H*-pyran-2-ones with 6,7-dihydro-5*H*-benzothiophene-4-one **2** in high yields. Additionally, our methodology avoids the use of environmentally toxic thiols and provides expedient access to 1,2-unsubstituted naphthothiophenes, which are difficult to prepare by classical approaches.

The 2*H*-pyran-2-ones **1** used as parent precursors were conveniently prepared by the reaction of methyl 2-carbomethoxy-3,3-dimethylsulfanylacrylate with acetophenone in high yields as described earlier.[13] Our approach to substituted naphtho[*b*]thiophenes involved stirring an equimolar mixture of the 2*H*-pyran-2-one **1**, commercially available 6,7-dihydro-5*H*-benzothiophene-4-one **2** and powdered KOH in dry DMF at room temperature for 15–18 h as shown in Scheme 1. After completion, the reaction mixture was poured into ice-water and the solution was neutralized with 10% HCl. The crude product was purified by column chromatography to afford the corresponding naphtho[*b*]thiophenes **3a**–**e** in good yields. All the synthesized compounds were characterized by elemental and spectroscopic analyses.[14] The ^{1}H NMR spectrum of **3a** showed three sharp singlets at δ 2.48, 2.81 and 3.95 for a methyl sulfanyl group, two methylene groups and a methoxycarbonyl group, respectively. A multiplet in the range δ 7.08–7.48 was assigned to the eight methine protons. The presence of the carbonyl peak at 1727 cm^{-1} in the IR spectrum and the molecular ion peak at *m*/*z* 366 in the mass spectrum was in agreement with the proposed structure.

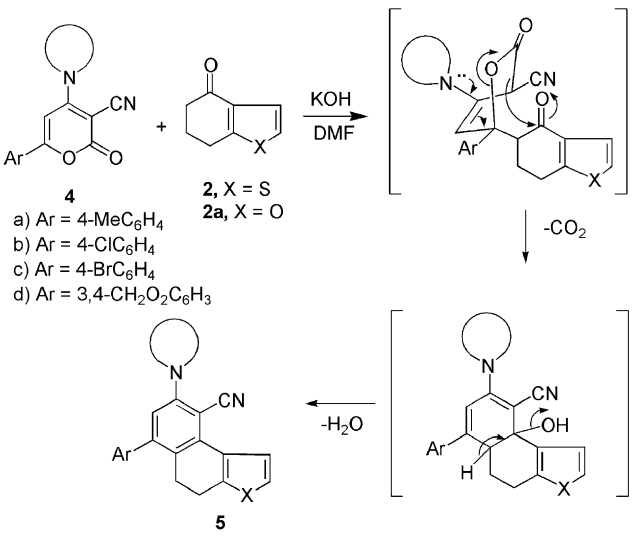
The mechanism, depicted in Scheme 1, implies that the reaction is initiated by attack of the carbanion generated in situ from 6,7-dihydro-5*H*-benzothiophene-4-one **2** at position C-6 of the pyran-2-one, followed by cyclization involving the carbonyl group and C-3 of the pyran ring to form a bicyclic intermediate. Finally, decarboxylation then dehydration yield products **3a**–**e** in good yields.

In order to demonstrate the synthetic utility and scope of this methodology for the regiospecific introduction of various functionalized amines and cyano substituents on the benzene ring of naphtho[*b*]thiophenes, we synthesized 6-aryl-2-oxo-4-amino-pyran-3-carbonitriles (**4a**–**d**) by replacing the methylsulfanyl group in 6-aryl-4-methylsulfanyl-2-oxo-pyran-3-carbonitriles with various secondary amines in methanol as described previously.[12b,13] Thus, the reaction of 2*H*-pyran-2-ones **4a**–**d** with cyclic ketone **2** was carried out as shown in Scheme 2. The reaction was monitored by TLC and after workup, we isolated 6-aryl-8-amino-4,5-dihydronaphtho[2,1-*b*]thiophene-9-carbonitriles **5a**–**e** in 75–89% yield.[15] In a further extension of these studies, naphtho[*b*]furans **5f**,**g** were synthesized in good yields in a similar fashion using 6,7-dihydro-5*H*-benzofuran-4-one[16] **2a** as shown in Scheme 2.



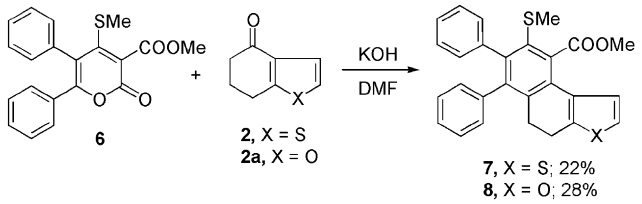
Entry	Ar	Reaction Time (h)	Melting Point (°C)	Yield (%) **3**
a	C_6H_5	16	139-140	67
b	4-FC_6H_4	15	161-162	73
c	4-ClC_6H_4	16	178-179	91
d	4-BrC_6H_4	16	180-181	78
e	4-$CH_3C_6H_4$	18	142-143	79

Scheme 1.



5	Ar	N	X	Yield (%)
a	4-MeC_6H_4	piperidine	S	89
b	4-ClC_6H_4	piperidine	S	86
c	4-BrC_6H_4	pyrrolidine	S	75
d	4-ClC_6H_4	4-methylpiperidine	S	83
e	4-MeC_6H_4	*N*-phenylpiperazine	S	79
f	4-ClC_6H_4	4-methylpiperidine	O	82
g	3,4-$CH_2O_2C_6H_3$	piperidine	O	73

Scheme 2.



Scheme 3.

The importance[17] of naphtho[*b*]thiophene-based diphosphanes as ligands for homogeneous stereoselective catalysis and diarylated benzo[*b*]thiophenes and naphtho[*b*]pyrans as novel photochromic materials prompted us to further extend the lactone methodology for preparing 6,7-diarylated-naphtho[*b*]thiophenes, which have not been synthesized prior to this study. Thus, reaction of 4-methylsulfanyl-2-oxo-5,6-diphenyl-2*H*-pyran-3-carboxylic acid methyl ester **6** (prepared from deoxybenzoin and methyl 2-carbomethoxy-3,3-dimethylsulfanylacrylate) with **2** was carried out as shown in Scheme 3. After a certain period of time, the reaction did not proceed further even after prolonged stirring for 48 h as monitored by TLC. Following workup and purification by column chromatography, we isolated 6,7-diphenyl-8-methylsulfanyl-4,5-dihydronaphtho[2,1-*b*]-thiophene-9-carboxylic acid methyl ester **7** in 22% yield together with unreacted lactone **6** (48%). The reaction was further explored by preparing diarylated-naphtho[2,1-*b*]furan **8** through the reaction of **6** with **2a** under similar reaction conditions. The ease of the preparation of these hindered diarylated systems in a single step opens a new avenue for further exploration.

In summary, we have demonstrated an efficient regioselective synthesis of diversely functionalized naphtho[*b*]thiophenes in a single step from easily accessible precursors in good yields. Our synthetic approach has several advantages including mild reaction conditions, versatility and compatibility of functional groups, use of inexpensive reagents and an easy workup process.

Acknowledgements

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14. Typical procedure for the synthesis of **3a**–**e**: A mixture of 3-carbomethoxy-4-methylsulfanyl-6-phenyl-2*H*-pyran-2-one (0.276 g, 1 mmol), 6,7-dihydro-5*H*-benzothiophene-4-one (0.16 g, 1.1 mmol) and powdered KOH (84 mg, 1.5 mmol) in dry DMF (5 mL) was stirred at room temperature for 15–18 h. After completion of the reaction, the mixture was poured onto crushed ice with vigorous stirring, then neutralized with 10% HCl. The precipitate thus obtained was filtered off, washed with water, dried and purified by silica gel column chromatography using chloroform–hexane (1:9) as eluent. Compound **3a**: MS (FAB): *m*/*z* 366 (M^+); IR (KBr) 1727 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ 2.48 (s, 3H, SCH_3), 2.81 (s, 4H, $2CH_2$), 3.95 (s, 3H, OCH_3), 7.08–7.48 (m, 8H, ArH); Anal. Calcd for $C_{21}H_{18}O_2S_2$: C, 68.82; H, 4.95. Found: C, 68.91; H, 4.91. Compound **3b**: MS (FAB): *m*/*z* 384 (M^+); IR (KBr) 1724 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ 2.48 (s, 3H, SCH_3), 2.80 (s, 4H, $2CH_2$), 3.95 (s, 3H, OCH_3), 7.09–7.33 (m, 7H, ArH). Compound **3c**: MS (FAB): *m*/*z* 402 (M^++2), 400 (M^+); IR (KBr) 1730 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ 2.48 (s, 3H, SCH_3), 2.80 (s, 4H, $2CH_2$), 3.95 (s, 3H, OCH_3), 7.07–7.24 (m, 5H, ArH), 7.42 (d, $J = 8.2$ Hz, 2H, ArH). Compound **3d**: MS (FAB): *m*/*z* 446 (M^++2), 444 (M^+); IR (KBr) 1728 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ 2.48 (s, 3H, SCH_3),

2.80 (s, 4H, $2CH_2$), 3.95 (s, 3H, OCH_3), 7.08–7.20 (m, 5H, ArH), 7.58 (d, $J = 8.2$ Hz, 2H, ArH). Compound **3e**: MS (FAB): m/z 380 (M^+); IR (KBr) 1727 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 2.48 (s, 3H, SCH_3), 2.80 (s, 4H, $2CH_2$), 3.95 (s, 3H, OCH_3), 7.03–7.35 (m, 7H, ArH).

15. Typical procedure for the synthesis of **5a**–**e**: A mixture of 6-aryl-2-oxo-4-amino-pyran-3-carbonitrile (1 mmol), 6,7-dihydro-5*H*-benzothiophene-4-one (0.16 g, 1.1 mmol) and powdered KOH (84 mg, 1.5 mmol) in dry DMF (5 mL) was stirred at room temperature for 12–20 h. After completion of the reaction, the mixture was poured onto crushed ice with vigorous stirring, then neutralized with 10% HCl. The precipitate thus obtained was filtered off, washed with water, dried and purified by silica gel column chromatography using 15% chloroform in hexane as eluent. Compound **5a**: mp: 148–149 °C; MS (FAB): m/z 384 (M^+); IR (KBr) 2209 cm^{-1} (CN); ^1H NMR (200 MHz, $CDCl_3$): δ 1.58–1.66 (m, 2H, CH_2), 1.73–1.88 (m, 4H, $2CH_2$), 2.42 (s, 3H, CH_3), 2.79 (s, 4H, $2CH_2$), 3.10–3.15 (m, 4H, $2CH_2$), 6.78 (s, 1H, ArH), 7.16–7.28 (m, 5H, CH, ArH), 8.14 (d, 1H, $J = 5.4$ Hz, CH); HR-EI-MS (M^+) m/z calculated for $C_{25}H_{24}N_2S$ 384.1660, Found: 384.1660. Compound **5b**: mp: 188–189 °C; MS (FAB): m/z 404 (M^+); IR (KBr) 2213 cm^{-1} (CN); ^1H NMR (200 MHz, $CDCl_3$): δ 1.58–1.66 (m, 2H, CH_2), 1.78–1.85 (m, 4H, $2CH_2$), 2.70–2.79 (m, 4H, CH_2), 3.08–3.18 (m, 4H, $2CH_2$), 6.70 (s, 1H, ArH), 7.13–7.27 (m, 3H, CH, ArH), 7.40 (d, 2H, $J = 8.4$ Hz, ArH), 8.10 (d, 1H, $J = 5.4$ Hz, CH); ^{13}C (50.32 MHz, $CDCl_3$) 23.95, 24.51, 26.63, 27.51, 54.30, 102.11, 118.69, 119.57, 122.20, 126.40, 127.45, 129.01, 130.59, 133.46, 134.23, 137.73, 139.83, 142.16, 145.29, 157.27; HR-EI-MS (M^+) m/z calculated for $C_{24}H_{21}ClN_2S$ 404.1114. Found: 404.1109. Compound **5c**: mp: 183–185 °C; MS (FAB): m/z 436 (M^++2), 434 (M^+); IR (KBr) 2202 cm^{-1} (CN); ^1H NMR (200 MHz, $CDCl_3$): δ 1.98–2.02 (m, 4H, $2CH_2$), 2.65–2.70 (m, 2H, CH_2), 2.72–2.78 (m, 2H, CH_2), 3.56–3.60 (m, 4H, $2CH_2$), 6.47 (s, 1H, ArH), 7.16–7.28 (m, 3H, CH, ArH), 7.56 (d, 2H, $J = 8.2$ Hz, ArH), 8.05 (d, 1H, $J = 5.4$ Hz, CH). Compound **5d**: mp: 209–210 °C; MS (FAB): m/z 418 (M^+); IR (KBr) 2217 cm^{-1} (CN); ^1H NMR (200 MHz, $CDCl_3$): δ 1.04 (d, 3H, $J = 5.2$ Hz, CH_3), 1.43–1.82 (m, 5H, CH, $2CH_2$), 2.66–2.85 (m, 6H, $3CH_2$), 3.48–3.58 (m, 2H, CH_2), 6.72 (s, 1H, ArH), 7.12–7.32 (m, 3H, CH, ArH), 7.39 (d, 2H, $J = 8.2$ Hz, ArH), 8.09 (d, 1H, $J = 5.2$ Hz, CH). Compound **5e**: mp: 179–180 °C; MS (FAB): m/z 461 (M^+); IR (KBr) 2217 cm^{-1} (CN); ^1H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 2.81 (s, 4H, $2CH_2$), 3.32–3.46 (m, 8H, $4CH_2$), 6.84 (s, 1H, ArH), 6.88–6.92 (m, 1H, CH), 6.99 (d, 2H, $J = 8.2$ Hz, ArH), 7.17–7.33 (m, 6H, ArH), 8.14 (d, 2H, $J = 5.2$ Hz, CH). Compound **5f**: mp: 166–168 °C; MS (ESI): m/z 403 (M^++1); IR (KBr) 2215 cm^{-1} (CN); ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 3H, CH_3), 1.47–1.60 (m, 3H, CH, CH_2), 1.70–1.81 (m, 2H, CH_2), 2.70–2.86 (m, 6H, $3CH_2$), 3.45–3.58 (m, 2H, CH_2), 6.64 (s, 1H, ArH), 7.22 (d, 2H, $J = 8.4$ Hz, ArH), 7.38 (d, 1H, $J = 2.0$ Hz, CH), 7.42 (d, 2H, $J = 8.4$ Hz, ArH), 7.48 (d, 1H, $J = 2.0$ Hz, CH). Compound **5g**: mp: 185–187 °C; MS (ESI): m/z 399 (M^++1); IR (KBr) 2207 cm^{-1} (CN); ^1H NMR (200 MHz, $CDCl_3$), δ 1.54–1.62 (m, 2H, CH_2), 1.72–1.81 (m, 4H, $2CH_2$), 2.70–2.81 (m, 2H, CH_2), 2.83–2.96 (m, 2H, CH_2), 3.04–3.14 (m, 4H, $2CH_2$), 6.02 (s, 2H, OCH_2O), 6.67 (s, 1H, ArH), 6.70–6.76 (m, 2H, ArH), 6.88 (d, 1H, $J = 7.8$ Hz, ArH), 7.38 (d, 1H, $J = 2.0$ Hz, CH), 7.48 (d, 1H, $J = 2.0$ Hz, CH). Compound **7**: mp: 254–256 °C; MS (ESI): m/z 442 (M^+); IR (KBr) 1724 cm^{-1} (CO); ^1H NMR (200 MHz, $CDCl_3$): δ 1.99 (s, 3H, CH_3), 2.60–2.70 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 3.95 (s, 3H, OCH_3), 6.88–7.00 (m, 4H, ArH), 7.05–7.25 (m, 8H, ArH). Compound **8**: mp: 222–224 °C; MS (ESI): m/z 426 (M^+); IR (KBr) 1733 cm^{-1} (CO), ^1H NMR (200 MHz, $CDCl_3$): 1.98 (s, 3H, SMe), 2.75 (s, 4H, $2CH_2$), 3.99 (s, 3H, OMe), 6.47 (d, 1H, $J = 2.0$ Hz, CH); 6.85–7.01 (m, 4H, ArH), 7.03–7.15 (m, 6H, ArH), 7.29 (d, 1H, $J = 2.0$ Hz, CH).

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