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SYNTHESIS OF 3-IMINOBENZO[*c*]THIOPHEN-1(3*H*)-ONE DERIVATIVES BASED ON THE REACTION OF 2-LITHIO-*N*,*N*-DIMETHYLBENZAMIDES WITH ISOTHIOCYANATES

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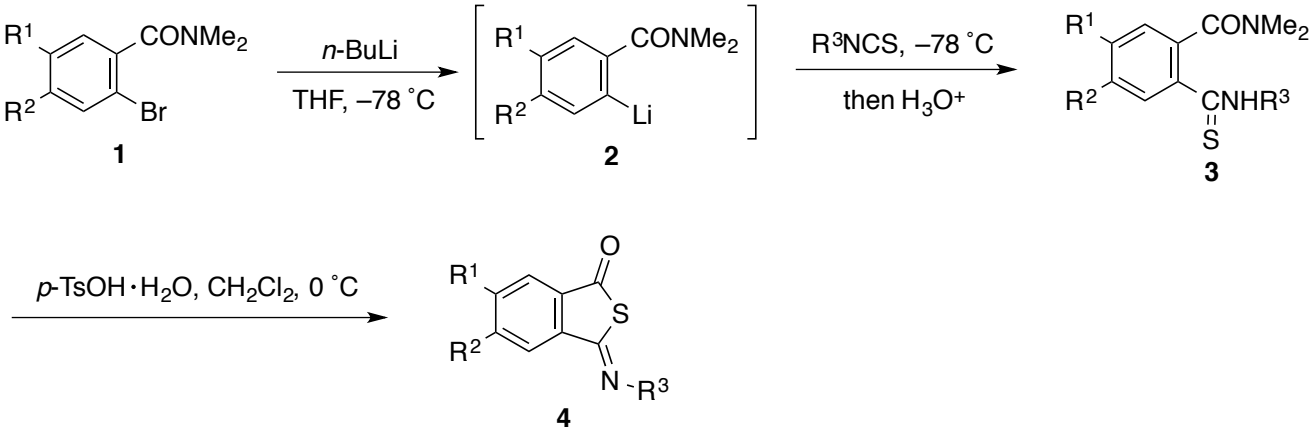
Abstract – A facile two-step sequence for the preparation of 3-(*Z*)-(aryl(or alkyl)imino)benzo[*c*]thiophen-1(3*H*)-ones starting from 2-bromo-*N*,*N*-dimethylbenzamides has been developed. The starting amides were allowed to react with butyllithium to generate 2-lithio-*N*,*N*-dimethylbenzamides, of which reaction with isothiocyanates gave the corresponding *N*,*N*-dimethyl-2-(thiocarbamoyl)benzamides. These precursors were treated with *p*-toluenesulfonic acid monohydrate. The cyclization proceeds in a chemo- and stereo-selective manner to provide the desired product as the sole isolated product in each case.

Benzo[*c*]thiophen-1(3*H*)-one derivatives have attracted significant attention because of their biological interests[1] and synthetic utilities.[2] So, several efficient syntheses of this class of compounds have been reported.[3] On the other hand, a number of methods for the general preparation of benzo[*c*]thiophen-1(3*H*)-imine derivatives have also been reported due to their synthetic importance.[4] We therefore became interested in the development of general method for the preparation of benzo[*c*]thiophen-1(3*H*)-one derivatives carrying an aryl(or alkyl)imino function at the 3-position, because these derivatives are of potentially biological and synthetic interest but only one derivative has been synthesized so far.[5] In this paper, we report the results of our investigation, which realizes the general preparation of such compounds. Our method is shown in Scheme 1 using readily available 2-bromo-*N*,*N*-dimethylbenzamides (**1**) as the starting materials.

The requisite starting materials (**1**) were readily available from the reaction of 2-bromobenzoyl chlorides and dimethylamine.[6] The bromine/lithium exchange between the starting materials **1** and butyllithium in

THF at –78 ˚C generating 2-lithio-*N*,*N*-dimethylbenzamides intermediates (**2**) and subsequent addition of isothiocyanates provided, after aqueous workup, *N*,*N*-dimethyl-2-(thiocarbamoyl)benzamides (**3**).



Scheme 1

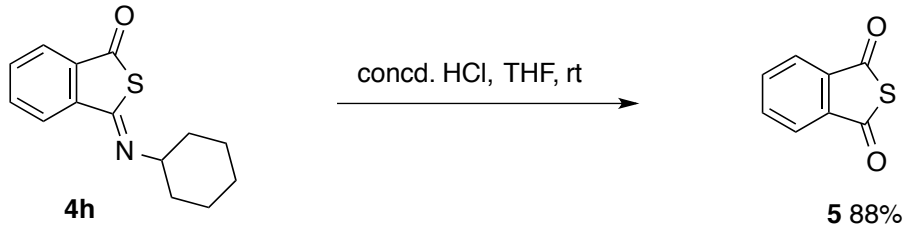
The next step in the synthesis of 3-(*Z*)-aryl(or alkyl)iminobenzo[*c*]thiophen-1(3*H*)-ones (**4**) was acid-mediated cyclization of **3**. Thus, these crude products (**3**) were without any purification subjected to treatment with an equimolar amount of *p*-toluenesulfonic acid monohydrate in dichloromethane at 0 ˚C, wherein thiolactonization occurred rapidly with complete chemo- and stereo-selectivities to give **4** in generally moderate-to-fair overall yields from **1** as compiled in Table 1, though the yield of cyclohexylimino derivative (**4h**) was rather lower (Entry 8). The lower yield of **4h** is probably due to the low reactivity of cyclohexyl isothiocyanate toward the lithium compound (**2a**). This highly chemoselectivity may be attributed to the higher nucleophilicity of sulfur than nitrogen. The configuration of 3-aryl(or alkyl)imino moiety of the products was assumed to be Z on the basis of NOESY analyses. For example, no interaction was observed between the ortho protons of *N*-phenyl ring and H(4) of the benzo[*c*]thiophene ring in compound (**4a**).

Table 1. Preparation of *N*-substituted 3-imino-1*H*-benzo[*c*]thiophen-1-ones (**4**)

Entry	**1**	R^1	R^2	R^3	**4**	Yield/%[a]
1	**1a**	H	H	Ph	**4a**	62
2	**1a**	H	H	2-MeC_6H_4	**4b**	59
3	**1a**	H	H	3-MeC_6H_4	**4c**	57
4	**1a**	H	H	4-ClC_6H_4	**4d**	60
5	**1a**	H	H	4-Cl-2-MeC_6H_3	**4e**	62
6	**1a**	H	H	3-$MeOC_6H_4$	**4f**	61
7	**1a**	H	H	naphthalen-2-yl	**4g**	53
8	**1a**	H	H	*c*-Hex	**4h**	36
9	**1b**	Cl	H	Ph	**4i**	50
10	**1c**	OMe	OMe	Ph	**4j**	50

[a] Yields of isolated products.

Acid hydrolysis of compound (**4h**) was carried out in order to confirm the 3-iminobenzo[*c*]thiophen-1(3*H*)-one structure of the products (**4**). Compound (**4h**) was hydrolyzed with concentrated hydrochloric acid in THF at room temperature to give benzo[*c*]thiphene-1,3-dione (**5**)[7,8] in 88% yield, as shown in Scheme 2.



4h **5** 88%

Scheme 2

In conclusion, a convenient strategy for the preparation of 3-iminobenzo[*c*]thophen-1(3*H*)-one derivatives has been developed. The method may be of value in organic synthesis because of the readily availability of the starting materials and the easy experimental operations and may offer pharmacophores of significant interest.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer Spectrum 65 FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 and 125 MHz, respectively. High-resolution MS spectra were measured by a JEOL JMS-T100GCV (EI, TOF; 70eV) spectrometer. Elemental analyses were performed with an Elementar Vario EL II instrument. TLC was carried out on Merck Kieselgel 60 PF_{254}. Column chromatography was performed using WAKO GEL C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 2-Bromo-*N*,*N*-dimethylbenzamide (**1a**)[6] was prepared according to the reported procedure. Butyllithium was supplied by Asia Lithium Corporation. All other chemicals used in this study were commercially available.

2-Bromo-*N*,*N*-dimethylbenzamides (1b) and (1c). These compounds were prepared from the respective acid chlorides[9,10] according to the procedure for the preparation of **1a**.

2-Bromo-5-chloro-*N*,*N*-dimethylbenzamides (1b): yield: 66%; a colorless viscous oil; R_f 0.35 (Et_2O/hexane 1:1); IR (neat) 1631 cm^{-1}; ^{1}H NMR δ 2.88 (s, 3H), 3.13 (s, 3H), 7.22 (dd, J = 8.6, 2.3 Hz,

1H), 7.26 (d, *J* = 2.3 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR δ 34.66, 38.10, 117.03, 130.26, 133.91, 133.96, 139.94, 167.72. HR-MS (EI). Calcd for $C_9H_9BrClNO$ (M): 260.9556. Found: *m*/*z* 260.9546.

2-Bromo-4,5-dimethoxy-*N*,*N*-dimethylbenzamides (1c): yield; 63%; a pale-yellow viscous oil; R_f 0.34 (AcOEt). The ^{1}H NMR data for this compound were identical those reported previously.[11]

Typical Procedure for the Preparation of 3-(*Z*)-(Aryl(or alkyl)imino)benzo[*c*]thiophen-1(3*H*)-ones (4). 3-(*Z*)-(Phenylimino)benzo[*c*]thiophen-1(3*H*)-one (4a). To a stirred solution of **1** (0.23 g, 1.0 mmol) in THF (6 mL) at –78 °C was added *n*-BuLi (1.6 M in hexane; 1.0 mmol) dropwise. After 15 min, PhNCS (0.14 g, 1.0 mmol) was added and stirring was continued for an additional 5 min before addition of saturated aqueous NH_4Cl (15 mL). The mixture was extracted with AcOEt (3 × 10 mL), and the combined extracts were washed with brine (10 mL), dried (Na_2SO_4) and concentrated by evaporation. The residue was dissolved in CH_2Cl_2 (4 mL) and to this solution *p*-TsOH·H_2O (0.19 g, 1.0 mmol) was added at 0 °C under stirring. After 10 min, anhydrous K_2CO_3 (0.5 g) was added and the mixture was stirred for 30 min. The mixture was filtered under reduced pressure and the filtrated was concentrated by evaporation. The residue was purified by column chromatography on SiO_2 (AcOEt/hexane 1:10) to give **4a** (0.15 g, 62%); a yellow solid; mp 79–80 °C (hexane/CH_2Cl_2); IR (KBr) 1701, 1628 cm^{-1}; ^{1}H NMR δ 7.12 (dd, *J* = 7.4, 1.1 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.78 (td, *J* = 7.4, 1.1 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 8.28 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 120.34, 123.37, 123.64, 126.08, 129.22, 132.40, 134.39, 136.47, 142.08, 150.41, 158.48, 191.61. HR-MS (EI). Calcd for $C_{14}H_9NOS$ (M): 239.0405. Found: *m*/*z* 239.0393. Anal Calcd for $C_{14}H_9NOS$: C, 70.27; H, 3.79; N, 5.85. Found: C, 70.21; H, 3.93; N, 5.73.

3-(*Z*)-[(2-Methylphenyl)imino]benzo[*c*]thiophen-1(3*H*)-one (4b): a yellow solid; mp 92–94 °C (hexane/CH_2Cl_2); IR (KBr) 1701, 1635 cm^{-1}; ^{1}H NMR δ 2.25 (s, 3H), 6.92 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.19–7.27 (m, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.79 (t, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 8.30 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 17.81, 118.19, 123.38, 123.59, 125.98, 126.55, 130.60, 132.35, 133.53, 134.37, 136.69, 141.86, 149.42, 158.19, 191.61. HR-MS (EI). Calcd for $C_{15}H_{11}NOS$ (M): 253.0561. Found: *m*/*z* 253.0567. Anal Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53. Found: C, 71.60; H, 4.49; N, 5.28.

3-(*Z*)-[(3-Methylphenyl)imino]benzo[*c*]thiophen-1(3*H*)-one (4c): yellow needles; mp 111–112 °C (hexane/CH_2Cl_2); IR (KBr) 1701, 1639 cm^{-1}; ^{1}H NMR δ 2.39 (s, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 7.30 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 8.27 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 21.44, 117.20, 121.04, 123.31, 123.60, 126.86, 129.03, 132.30, 134.33, 136.49, 139.16, 142.12, 150.42, 158.13, 191.70. HR-MS (EI). Calcd for $C_{15}H_{11}NOS$ (M): 253.0561. Found: *m*/*z* 253.0550. Anal Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53; S, 12.66. Found: C, 71.07; H, 4.40; N, 5.53; S, 12.45.

3-(*Z*)-[(4-Chlorophenyl)imino]benzo[*c*]thiophen-1(3*H*)-one (4d): an orange solid; mp 185–187 ˚C (hexane/CH_2Cl_2); IR (KBr) 1755, 1605 cm^{-1}; ^1H NMR δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.77–7.82 (m, 2H), 7.88–7.89 (m, 1H), 8.07–8.09 (m, 1H); ^{13}C NMR δ 123.25, 124.45, 126.70, 129.38, 129.69, 131.94, 133.71, 134.54, 134.86, 137.03, 169.08, 196.74. HR-MS (EI). Calcd for $C_{14}H_8ClNOS$ (M): 273.0015. Found: *m*/*z* 273.0005. Anal Calcd for $C_{14}H_8ClNOS$: C, 61.43; H, 2.95; N, 5.12; S, 11.71. Found: C, 61.32; H, 3.12; N, 5.07; S, 11.85.

3-(*Z*)-[(4-Chloro-2-methylphenyl)imino]benzo[*c*]thiophen-1(3*H*)-one (4e): a yellow solid; mp 155–157 ˚C (hexane/CH_2Cl_2); IR (KBr) 1701, 1634 cm^{-1}; ^1H NMR δ 2.19 (s, 3H), 6.92 (d, *J* = 1.7 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 8.28 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 17.27, 118.33, 123.57, 123.62, 125.63, 127.82, 131.68, 131.77, 132.66, 134.51, 136.72, 141.60, 150.33, 159.72, 190.79. HR-MS (EI). Calcd for $C_{15}H_{10}ClNOS$ (M): 287.0172. Found: *m*/*z* 287.0171. Anal Calcd for $C_{15}H_{10}ClNOS$: C, 62.61; H, 3.50; N, 4.87. Found: C, 62.44; H, 3.48; N, 4.87.

3-(*Z*)-[(3-Methoxyphenyl)imino]benzo[*c*]thiophen-1(3*H*)-one (4f): a yellow solid; mp 77–79 ˚C (hexane/CH_2Cl_2); IR (KBr) 1707, 1633 cm^{-1}; ^1H NMR δ 3.83 (s, 3H), 6.66 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.80 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 8.27 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 55.36, 106.02, 111.95, 112.47, 123.38, 123.65, 130.07, 132.42, 134.38, 136.55, 142.06, 151.69, 158.71, 160.26, 191.55. HR-MS (EI). Calcd for $C_{15}H_{11}NO_2S$ (M): 269.0510. Found: *m*/*z* 269.0503. Anal Calcd for $C_{15}H_{11}NO_2S$: C, 66.90; H, 4.12; N, 5.20. Found: C, 66.77; H, 4.13; N, 5.14.

3-(*Z*)-[(Naphthalen-2-yl)imino]benzo[*c*]thiophen-1(3*H*)-one (4g): a yellow solid; mp 136–138 ˚C (hexane/CH_2Cl_2); IR (KBr) 1696, 1627, 1611 cm^{-1}; ^1H NMR δ 7.32 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.46–7.53 (m, 3H), 7.70 (td, *J* = 7.4, 1.1 Hz, 1H), 7.80 (td, *J* = 7.4, 1.1 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 8.33 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 117.15, 120.70, 123.41, 123.70, 125.82, 126.72, 127.81, 128.01, 129.26, 131.69, 132.45, 133.63, 134.43, 136.49, 142.13, 148.10, 158.75, 191.61. HR-MS (EI). Calcd for $C_{18}H_{11}NOS$ (M): 289.0561. Found: *m*/*z* 289.0553. Anal. Calcd for $C_{18}H_{11}NOS$: C, 64.20; H, 4.38; N, 4.68. Found: C, 64.08; H, 4.29; N, 4.53.

3-(*Z*)-(Cyclohexylimino)benzo[*c*]thiophen-1(3*H*)-one (4h): a colorless oil; R_f 0.32 (AcOEt/hexane 1:15); IR (neat) 1704, 1634 cm^{-1}; ^1H NMR δ 1.26–1.45 (m, 3H), 1.60–1.74 (m, 3H), 1.84–1.86 (m, 4H), 3.30–3.36 (m, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 24.24, 25.46, 33.07, 68.36, 123.07, 123.50, 131.42, 134.04, 136.71, 142.41, 153.66, 191.26. HR-MS (EI). Calcd for $C_{14}H_{15}NOS$ (M): 245.0874. Found: *m*/*z* 245.0869. Anal. Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71. Found: C, 68.47; H, 6.30; N, 5.59.

6-Chloro-3-(*Z*)-(phenylimino)benzo[*c*]thiophen-1(3*H*)-one (4i): an orange solid; mp 192–195 °C (hexane/CH_2Cl_2); IR (KBr) 1751, 1607 cm^{-1}; ^1H NMR δ 7.35 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.49 (tt, *J* = 7.4, 1.7 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.72 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.84 (d, *J* = 1.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR δ 123.31, 125.61, 128.29, 128.41, 129.14, 129.18, 133.31, 134.38, 135.12, 140.30, 168.20, 195.67. HR-MS (EI). Calcd for $C_{14}H_8ClNOS$ (M): 273.0015. Found: *m/z* 273.0005. Anal. Calcd for $C_{14}H_8ClNOS$: C, 61.43; H, 2.95; N, 5.12. Found: C, 61.23; H, 3.01; N, 5.16.

5,6-Dimethoxy-3-(*Z*)-(phenylimino)benzo[*c*]thiophen-1(3*H*)-one (4j): an orange solid; mp 206–208 °C (hexane/CH_2Cl_2); IR (KBr) 1725, 1596 cm^{-1}; ^1H NMR δ 4.03 (s, 3H), 4.05 (s, 3H), 7.29 (s, 1H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.49 (s, 1H), 7.53 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR δ 56.66, 56.73, 104.54, 106.16, 120.05, 128.45, 128.76, 129.03, 131.68, 133.78, 153.94, 154.11, 169.38, 197.14. HR-MS (EI). Calcd for $C_{16}H_{13}NO_3S$ (M): 299.0616. Found: *m/z* 299.0612. Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38; N, 4.68. Found: C, 64.19; H, 4.50; N, 4.39.

Benzo[*c*]thiophene-1,3-dione (5).[7] To a solution of **4h** (88 mg, 0.36 mmol) in THF (2 mL) was added concentrated HCl (0.2 mL) and the solution was stirred for 1 h at rt. Saturated aqueous $NaHCO_3$ (15 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). The combined extracts were washed with brine (10 mL), dried (Na_2SO_4) and concentrated by evaporation. The residual solid was recrystallized from hexane/CH_2Cl_2 to give **5** (52 mg, 88%); mp 112–114 °C (lit.,[7] 114 °C). The spectral (IR, ^1H NMR) data for this compound were identical to those reported previously.[8]

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