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ScienceDirect
Tetrahedron 63 (2007) 10276–10281
Tetrahedron

Iodine-mediated cyclisation of thiobenzamides to produce benzothiazoles and benzoxazoles

Nadale K. Downer-Riley and Yvette A. Jackson*

Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

Received 26 March 2007; revised 7 July 2007; accepted 20 July 2007
Available online 29 July 2007

Abstract—Synthesis of benzothiazoles by reaction of iodine with thiobenzamides, which do not possess an *ortho* alkoxy or ester group, is described. The unlikely synthesis of benzoxazoles from reaction of 2-alkoxythiobenzamides with iodine is also reported.

1. Introduction

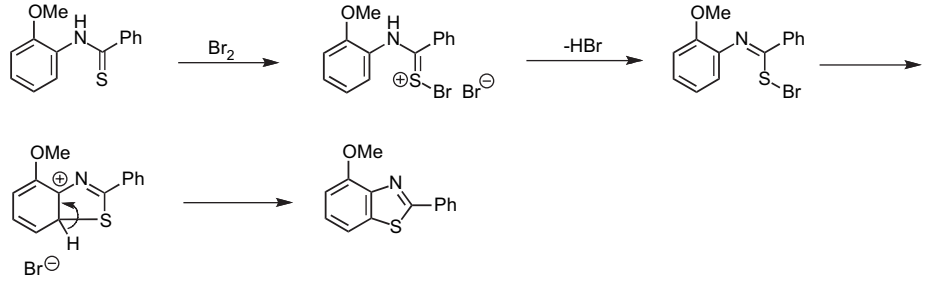
Synthesis of 2-substituted benzothiazoles is of interest due to their cyctotoxicity as well as their possible use as precursors to pharmacologically active natural products.[1,2] Among the methods of synthesis of these benzothiazoles, cyclisation of the corresponding thiobenzamides has received much attention, and varying reagents—Dess–Martin periodinane, manganese triacetate, radiation, tributyltin hydride and AIBN, NaH and NMP, potassium carbonate in acetone, palladium, copper, butyllithium, potassium ferricyanide with base—have been used.[3]

Bromine has also been used to good effect for this cyclisation, and in this case the reaction is thought to occur via a sulfenyl bromide, which is subsequently attacked by the π-system of the aromatic ring , similar to the pathway shown in Scheme 1.[4] Bromine is, however, a toxic and corrosive reagent. Furthermore, the measurement of stoichiometric amounts for small scale reactions is difficult and there is therefore a high risk of forming brominated side products. The use of benzyltrimethylammonium tribromide as an alternative to liquid bromine in the cyclisation of arylthioureas to 2-aminobenzothiazoles has since been reported, in which these disadvantages are eliminated.[5]

Iodine, which is available as a crystalline solid, is easier to handle and less toxic than liquid bromine. The ability of iodine to act as an oxidant as well as a Lewis acid has been exploited in the cyclisation of thiols and disulfides to produce benzothiophenes, dihydronaphthothiophenes, dihydronaphthopyrans and thiazinones.[6–8] The use of iodine in cyclisation of thiobenzamides to benzothiazoles, however, has not been reported. We set out to investigate this.

2. Results and discussion

We first explored the reaction of 2-methoxythiobenzamides with iodine. This reaction was expected to occur via the sulfenyl iodide, as in the reaction with bromine (Scheme 1). Cyclisation of arylthioureas with bromine in chloroform was found to require heating at reflux for 2.5 h.[5] After stirring a mixture of thiobenzamides **1**–**3** and iodine (2 mol



Scheme 1.

Keywords: Benzoxazoles; Benzothiazoles; Iodine-mediated cyclisation; Thiobenzamides.
* Corresponding author. E-mail: yvette.jackson@uwimona.edu.jm

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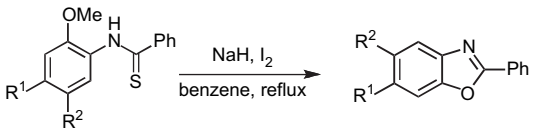
doi:10.1016/j.tet.2007.07.076

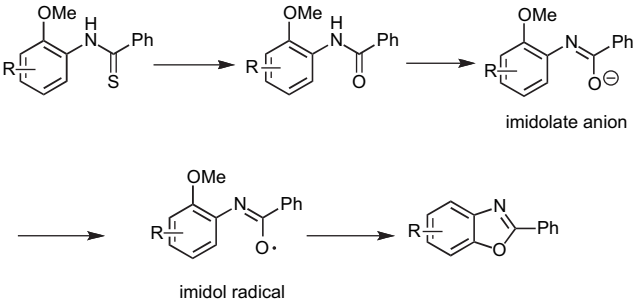
equiv) in refluxing chloroform, benzene or toluene for up to a day, however, only the starting material was recovered. This was thought to be due to lack of formation of the sulfenyl iodide. In order to promote formation of the sulfenyl iodide, NaH was added to a solution of each thiobenzamide in benzene followed by addition of iodine. Reaction of thiocarbonyls with a halogen in the presence of hydroxide ions is known to produce the corresponding carbonyl compound.[9] Scrupulously dry conditions were therefore maintained. In each case, a mixture of thiobenzamide **1a–c** and NaH (1.2 mol equiv) in dry benzene was heated at reflux for 15 min. Addition of iodine (2 mol equiv) to this mixture, and heating at reflux for a further 2 h, surprisingly, yielded the corresponding 2-phenylbenzoxazoles **2a–c** as the major product (Scheme 2).



1a $R^1 = R^2 = H$ — **2a** (95 %)
1b $R^1 = H$, $R^2 = OMe$ — **2b** (80 %)
1c $R^1 = R^2 = OMe$ — **2c** (39 %)

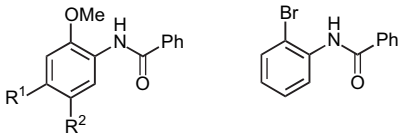
Scheme 2.

In our experience, the reaction of *o*-methoxythiobenzamides with AIBN brought about cyclisation to benzothiazoles, with loss of a methoxy group as a radical.[10] Reaction of thiobenzamides **1a–c** to produce benzoxazoles **2a–c** (Scheme 2), with loss of methoxy radical could occur via the imidol radical as shown in Scheme 3, but would suggest initial formation of the corresponding benzamide. Irradiation of 2-halogenobenzamides in alkaline solution has also been reported to yield benzoxazoles via an imidol radical.[11]



Scheme 3.

Benzamide formation should have been precluded by the dry reaction conditions. This was, however, investigated by treatment of benzamides **3a–d** with NaH/I_2 under similar conditions as for **1a–c**.

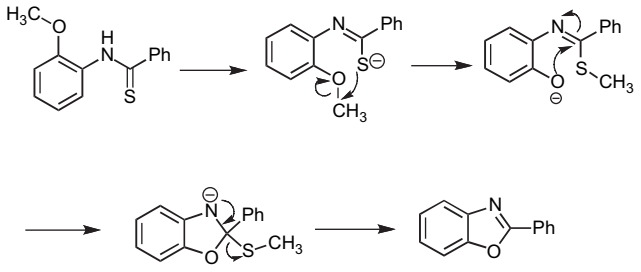


3a $R^1 = R^2 = H$
3b $R^1 = H$, $R^2 = OMe$
3c $R^1 = R^2 = OMe$

3d

These reactions, however, yielded only the starting material in the case of compounds **3b–d**, whereas 2-methoxybenzamide (**3a**) gave 2-phenylbenzoxazole (**1a**, 25%—identical to a sample prepared by condensation of *o*-aminophenol with benzoyl chloride), possibly via an addition–elimination reaction (Scheme 4).[12] The reluctance of 2-bromobenzamide (**3d**) to cyclise under these conditions indicated that the imidol radical was not being generated. It is also clear that reaction of **1a–c** as outlined in Scheme 2 does not involve initial conversion to the corresponding benzamide.

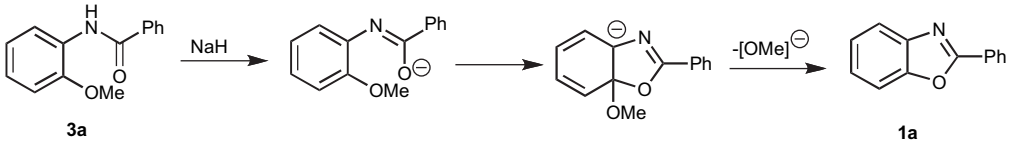
It seems, then, that in the NaH/I_2 cyclisation of thiobenzamides **1a–c** to benzoxazoles **2a–c**, the oxygen atom of the benzoxazole moiety is from the methoxy group *ortho* to the thiobenzamide functionality. Thiolate ions are known to effect demethylation of aryl alkyl ether.[2] If the thiolate anion, produced by reaction of thiobenzamide with base, was capable of demethylating the *ortho* methoxy group, the phenolate anion thus produced could go on to form the benzoxazole (Scheme 5).



Scheme 5.

In order to avoid the formation of thiolate anion, thiobenzamides **1a–c** were treated with iodine in the absence of base. Heating a solution of the thiobenzamides **1a–c** in chlorobenzene with 2 mol equiv iodine at reflux for 12 h produced, as in the case of the reaction with NaH/I_2 in benzene (Scheme 2), benzoxazoles **2a–c** in yields of 42–81% (Table 1). No reaction was observed when benzene or toluene was used as solvent.

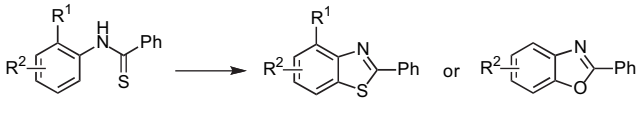
Thiolate anion formation and demethylation, therefore, were not necessary for benzoxazole formation. A rational mechanism for the iodine-mediated cyclisation of



3a **1a**

Scheme 4.

Table 1. Thiobenzamide cyclisation using iodine



9 **10** **2**

	R^1	R^2	NaH, I_2/benzene (% yield)	I_2/chlorobenzene (% yield)	I_2/nitrobenzene (% yield)
1a	OMe	H	**2a** (95)	**2a** (73)	—
1b	OMe	4-OMe	**2b** (80)	**2b** (81)	**2b** (83)
1c	OMe	4,5-OMe	**2c** (39)	**2c** (42)	**2c** (51)
8a	OEt	H	**2a** (96)	**2a** (83)	—
8b	O-*i*-Pr	H	**2a** (70)	**2a** (68)	—
8c	OTs	H	**2a** (76)	**2a** (40)	—
9a[2]	H	3-OMe	**10a** (67)	**10a** (56)	—
9b[2]	H	4-OMe	**10b** (27)	**10b** (70)	—
9c[2]	H	3,4-OMe	**10c** (87)	**10c** (73)	**10c** (84)
9d[12]	H	2-Br	[a]	[a]	[a]
9e[14]	H	H	[a]	[a]	[a]

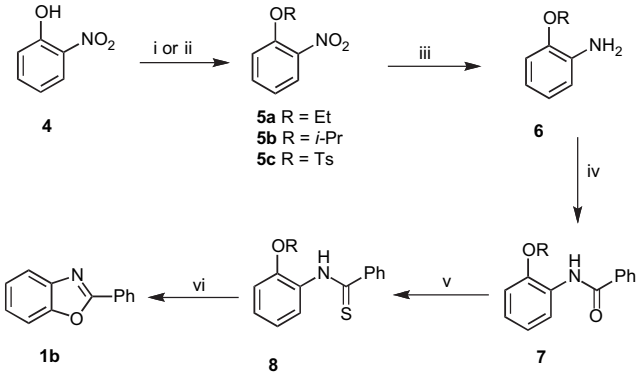
[a] Starting material was recovered from the reaction mixture.

o-methoxythiobenzamides has therefore been proposed. The sulfenyl iodide produced by reaction of iodine with thiobenzamide is probably attacked by the oxygen atom of the methoxy group, producing benzoxazole with loss of hydrogen iodide, methyl iodide and sulfur (Scheme 6).

Reaction with chlorobenzene/I_2 in benzene effected cyclisation in 12 h. Using chlorobenzene/TFA (4:1) or nitrobenzene as solvent lessened the reaction time to 2 h. Use of K_2CO_3 in place of NaH resulted only in conversion to the corresponding benzamides.

We also explored the reaction of 2-ethoxy- and 2-isopropoxythiobenzamides **8a**,**b** as well as *o*-thiobenzamide tosyl ester **8c** with iodine. Based on the mechanism proposed for benzoxazole formation from *o*-methoxythiobenzamides (Scheme 6), bulky alkyl groups (such as *tert*-butyl and isopropyl) could deter benzoxazole formation by preventing attack of the sulfenyl iodide by the *ortho* oxygen. In addition to being bulky, the tosyl group also reduces the nucleophilic nature of the oxygen, rendering the *ortho* oxygen less likely to attack the sulfenyl iodide. *o*-Ethoxythiobenzamide **8a** was expected to react similarly to *o*-methoxythiobenzamide **1**.

The desired thiobenzamides were synthesised from 2-nitrophenol (**4**) as shown in Scheme 7. *o*-Nitrophenol (**4**) was alkylated by reaction with the respective alkyl iodide and potassium carbonate in acetone and tosylated by reaction with *p*-toluenesulfonyl chloride in pyridine. The nitro compounds were then reduced using hydrogen and catalyst, condensed with benzoyl chloride and the resultant benzamide thionated using Lawesson's reagent. Attempted reaction of *o*-nitrophenol with *tert*-butyl iodide in a bid to synthesise *o-tert*-butoxythiobenzamide was unsuccessful.

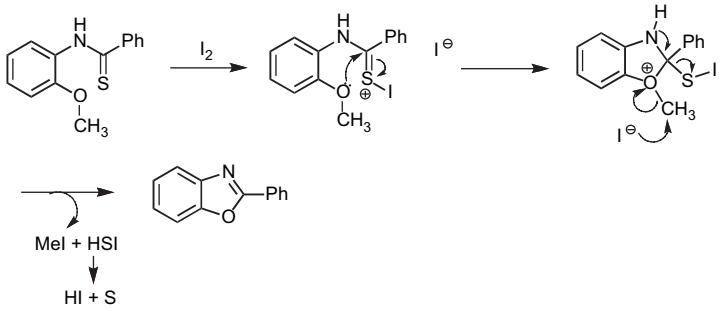


Scheme 7. Reagents: (i) MeI or *i*-PrI, K_2CO_3, acetone, reflux; (ii) *p*-TsCl, pyridine, 90 °C; (iii) H_2, Pd/C, MeOH; (iv) benzoyl chloride, pyridine, toluene, reflux; (v) Lawesson's reagent, toluene, reflux; (vi) NaH, I_2, benzene, reflux or I_2, chlorobenzene, reflux.

Reaction of the *o*-ethoxythiobenzamide **8a** and *o*-isopropoxythiobenzamide **8b** with iodine/chlorobenzene or iodine/NaH/benzene resulted in formation of 2-phenylbenzoxazole (**2a**) (68–96% yield). The *iso*-propoxy group did not hinder benzoxazole formation. Reaction of thiobenzamide **8c** with iodine/chlorobenzene and iodine/NaH/benzene also resulted in benzoxazole **2a** (76 and 40%, respectively, Table 1).

We considered this reaction of tosyl ester **8c** to be unusual, and thus subjected various tosyl esters, which do not possess the *o*-thiobenzamide moiety, to similar reaction with iodine. In all cases, only the starting material was recovered, indicating that detosylation was not a factor in formation of benzoxazoles from compound **8c**.

Based on these findings, it is apparent that cyclisation of thiobenzamides will not occur to give benzothiazoles when an *ortho* alkoxy or ester group is in place. We next explored the reaction of known thiobenzamides **9a**–**e**, which do not possess the *ortho* methoxy group, with iodine. The



Scheme 6.

corresponding benzothiazoles **10a–c** were obtained from thiobenzamides **9a–c** in yields of up to 87% after heating overnight with iodine in refluxing chlorobenzene or heating with sodium hydride and iodine in refluxing benzene for 2 h (Table 1). Treatment of thiobenzamides **9d** and **9e** with NaH and iodine in benzene, however, yielded the unconverted starting material. The primary rings of thiobenzamides **9d** and **9e** possess low electron densities and as such are unlikely to be involved in nucleophilic attack of the sulfenyl halide.

In conclusion, iodine has been found to be useful for the formation of benzothiazoles from thiobenzamides without an *ortho* alkoxy or ester group and formation of benzoxazoles from *ortho* alkoxythiobenzamides.

3. Experimental

3.1. General

IR spectra were obtained on a Perkin–Elmer 735B FTIR spectrometer as KBr discs. NMR spectra (Bruker 200 and 500 MHz) were obtained in $CDCl_3$ solution and the resonances are reported in δ units downfield from TMS as an internal standard; J values are given in hertz. Elemental analyses were carried out by MEDAC Ltd., Egham, Surrey, UK. Column chromatography was carried out using silica gel as adsorbent.

3.2. Alkylation of 2-nitrophenol (4)

To a solution of 2-nitrophenol (3.77 g, 27.1 mmol) in acetone (50 mL) was added potassium carbonate (3.77 g, 27.3 mmol) followed by alkyl iodide (1.2 mol equiv). The mixture was heated at reflux for 4 h, cooled and then filtered. The filtrate was poured into water (100 mL) and extracted with dichloromethane (100 mL). The organic extract was then dried (Na_2SO_4) and concentrated in vacuo to yield a light yellow oil: 2-ethoxynitrobenzene (**5a**)[15] (69%); 2-isopropoxynitrobenzene (**5b**)[15] (82%).

3.3. 2-Nitrophenyl 4-methylbenzenesulfonate (5c)

To a solution of 2-nitrophenol (4.05 g, 29.1 mmol) in pyridine (10 mL) was added *p*-toluenesulfonyl chloride (5.73 g, 30.0 mmol). The mixture was heated at 90 °C for 20 min after which the mixture was poured into cold water (200 mL). The resultant white solid was collected by filtration, washed with 3 M HCl (50 mL) followed by 5% aqueous NaOH (50 mL) and recrystallised from acetone/hexanes as white needles (6.40 g, 75%), mp 78–79 °C (acetone/hexanes) (lit.[16] 81–82 °C).

3.4. Reduction of nitro compounds

To a solution of the nitro compound (5.0 g) in methanol (150 mL) was added 10% Pd/C (0.25 g). The mixture was shaken in a Parr apparatus under an atmosphere of hydrogen (15 psi) for 4 h, filtered through Celite and concentrated to provide the corresponding aniline in quantitative yield. The aniline was recrystallised from ethyl acetate/hexanes.

3.4.1. 2-Ethoxyaniline (6a). Isolated as a purple oil (lit.[17] bp, 224–229 °C).

3.4.2. 2-Isopropoxyaniline (6b). Isolated as purple needles; mp 137–139 °C (lit.[18] 134–135 °C).

3.4.3. 2-Aminophenyl 4-methylbenzenesulfonate (6c). Isolated as light brown cubes; mp 94–96 °C; ν_{max}/cm^{-1} 3509, 3413, 1622; (Found: C, 59.00; H, 5.00; N, 5.32%. Calcd for $C_{13}H_{13}NO_3S$: C, 59.30; H, 4.98; N, 5.25%.) δ_H 2.46 (3H, s, CH_3), 3.54 (2H, s, NH_2), 6.60 (1H, m, 6-H), 6.75 (2H, m, 4,5-H), 7.02 (1H, m, 3-H), 7.32 (2H, d, J 8.3, tosyl), 7.78 (2H, d, J 8.2, tosyl); δ_C 21.7, 117.2, 118.3, 122.9, 127.8, 128.5, 129.8, 132.7, 137.0, 139.6, 145.5.

3.5. Preparation of benzamides

To a solution of the aniline (1.0 g) in dry toluene (6 mL) and pyridine (5 mL) was added benzoyl chloride (1.1 mol equiv). The mixture was heated at reflux for 1 h then poured into water (100 mL) and extracted with ethyl acetate (30 mL). The organic solution was washed with 1 M HCl (50 mL), 5% aqueous sodium bicarbonate (50 mL) then water (50 mL), dried (Na_2SO_4) and concentrated in vacuo.

3.5.1. *N*-(2-Ethoxyphenyl)benzamide (7a). Isolated as a yellow-brown oil, which was purified by column chromatography using CH_2Cl_2 as the eluent (85%, lit.[19] mp 104 °C); R_f (CH_2Cl_2) 0.73; ν_{max}/cm^{-1} 1656, 1605; δ_H 1.44 (3H, t, J 6.9, CH_3), 4.13 (2H, q, J 7.1, CH_2), 6.93 (1H, m, 3-H), 7.02 (1H, m, 5-H), 7.15 (1H, m, 4-H), 7.44 (3H, m, 3′,4′,5′-H), 7.83 (2H, m, 2′,6′-H), 9.18 (1H, m, 6-H), 9.73 (1H, s, N–H); δ_C 14.8, 64.5, 111.3, 120.3, 121.4, 126.4, 126.7, 128.6, 128.8, 130.9, 144.1, 149.2.

3.5.2. *N*-(2-Isopropoxyphenyl)benzamide (7b). Isolated as a yellow-brown oil, which was purified by column chromatography using CH_2Cl_2 as the eluent (98%); (Found: C, 75.20; H, 6.58; N, 5.27%. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%.) R_f (CH_2Cl_2) 0.80; ν_{max}/cm^{-1} 3426, 1788; δ_H 1.39 (6H, d, J 6.0, CH_3), 4.63 (1H, m, CH), 7.02 (1H, m, 3-H), 7.52 (3H, m, 3′,4′,5′-H), 7.88 (2H, m, 2′,6′-H), 8.14 (2H, m, 4,5-H), 8.57 (1H, m, 6-H), 8.69 (1H, s, N–H); δ_C 22.3, 71.5, 112.7, 119.9, 121.1, 123.8, 127.0, 128.9, 130.6, 131.7, 134.6, 146.4, 165.0.

3.5.3. 2-(Benzoylamino)phenyl 4-methylbenzenesulfonate (7c). Isolated as light brown cubes (87%), mp 105–106 °C (ethyl acetate/hexanes); (Found: C, 65.59; H, 4.61; N, 3.77%. Calcd for $C_{20}H_{17}NO_4S$: C, 65.38; H, 4.66; N, 3.81%.) ν_{max}/cm^{-1} 3328, 1677; δ_H 2.36 (3H, s, CH_3), 6.98 (2H, m, tosyl), 7.22 (3H, m, 3,4,5-H), 7.52 (3H, m, 3′,4′,5′-H), 7.68 (2H, m, tosyl), 7.83 (2H, m, 2′,6′-H), 8.38 (2H, m, 6-H and N–H); δ_C 21.7, 122.9, 123.1, 124.6, 127.1, 127.9, 128.4, 128.8, 130.1, 131.3, 131.5, 132.2, 134.1, 139.3, 146.3, 165.0.

3.6. Thionation of benzamides

To a solution of the benzamide (1.0 g) in dry toluene (40 mL) was added Lawesson's reagent (0.6 mol equiv). The mixture was heated at reflux under an atmosphere of nitrogen for 2 h, after which it was concentrated and purified

by column chromatography or recrystallised from methanol as yellow needles.

3.6.1. *N*-(2-Ethoxyphenyl)thiobenzamide (8a). Yield: 72%, mp 88–89 °C (methanol); (Found: C, 70.17; H, 5.88; N, 5.40%. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.45%.) ν_{max}/cm^{-1} 1607, 928; δ_H 1.44 (3H, t, *J* 6.9, CH_3), 4.13 (2H, q, *J* 7.0, CH_2), 6.93 (1H, m, 3-H), 7.02 (1H, m, 5-H), 7.15 (1H, m, 4-H), 7.44 (3H, m, 3′,4′,5′-H), 7.83 (2H, m, 2′,6′-H), 9.18 (1H, m, 6-H), 9.73 (1H, s, N–H); δ_C 14.8, 64.5, 111.3, 120.3, 121.4, 126.4, 126.7, 128.6, 128.8, 130.9, 144.1, 149.2.

3.6.2. *N*-(2-Isopropoxyphenyl)thiobenzamide (8b). Yield: 67%, mp 79–80 °C (methanol); (Found: C, 70.75; H, 6.32; N, 5.15%. Calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16%.) ν_{max}/cm^{-1} 3354, 2973; δ_H 1.35 (6H, d, *J* 5.7, CH_3), 4.62 (1H, m, CH), 6.96 (2H, m, 4,5-H), 7.14 (1H, d, *J* 8.3, 3-H), 7.43 (3H, m, 3′,4′,5′-H), 7.85 (2H, m, 2′,6′-H), 9.24 (1H, d, *J* 8.0, 6-H), 9.82 (1H, s, N–H); δ_C 22.3, 71.8, 112.8, 120.3, 121.3, 126.4, 126.7, 128.7, 131.1, 144.1, 148.1, 195.3.

3.6.3. 2-[(Phenylcarbonothioyl)amino]phenyl 4-methylbenzenesulfonate (8c). Yield: 73%, mp 121–123 °C (methanol); (Found: C, 62.62; H, 4.22; N, 3.58%. Calcd for $C_{20}H_{17}NO_3S_2$: C, 62.64; H, 4.47; N, 3.65%.) ν_{max}/cm^{-1} 3344, 1595, 1367; δ_H 2.43 (3H, s, CH_3), 7.03 (1H, m, 4-H), 7.17 (1H, m, 3-H), 7.25 (2H, m, tosyl), 7.33 (1H, m, 5-H), 7.47 (3H, m, 3′,4′,5′-H), 7.67 (2H, m, tosyl), 7.83 (2H, m, 2′,6′-H), 8.49 (1H, s, N–H), 9.43 (1H, m, 6-H); δ_C 21.8, 126.4, 126.9, 127.3, 127.4, 128.4, 128.6, 130.1, 131.5, 132.6, 146.3.

3.7. Cyclisation of thiobenzamides using iodine

Method 1: to a mixture of thiobenzamide (0.10 g) and NaH (1.2 mol equiv) under an atmosphere of nitrogen was added dry benzene (5 mL). The mixture was heated at reflux for 15 min after which a saturated solution of iodine (2 mol equiv) in dry benzene was added and the mixture heated at reflux for 2 h. The mixture was then poured into 15% aqueous sodium hydrogen sulfite solution (20 mL) and extracted with benzene (20 mL). The organic solution was then washed with water (20 mL), dried over Na_2SO_4, concentrated and purified by column chromatography (CH_2Cl_2/hexanes 3:7) and recrystallised from methanol as white needles.

Method 2: to a mixture of the thiobenzamide (0.10 g) and iodine (1.5 mol equiv) under an atmosphere of nitrogen was added chlorobenzene (3 mL). The mixture was heated at reflux for 12 h then poured into 15% aqueous sodium bisulfite solution (20 mL) and extracted with dichloromethane (20 mL). The organic solution was then washed with water (20 mL), dried over Na_2SO_4, concentrated and recrystallised from methanol.

Method 3: to a mixture of the thiobenzamide (0.10 g) and iodine (1.5 mol equiv) under an atmosphere of nitrogen was added nitrobenzene (3 mL). The mixture was heated at 200 °C for 1 h then placed on a silica column and eluted with hexanes to remove nitrobenzene and iodine and then with dichloromethane to obtain the benzoxazole. The benzoxazole was then recrystallised from methanol as white needles.

3.7.1. 2-Phenylbenzoxazole (2a).[12]

(a) Yield: 95 and 73% from **1a** using methods 1 and 2, respectively.
(b) Yield: 96 and 83% from **8a** using methods 1 and 2, respectively.
(c) Yield: 70 and 68% from **8b** using methods 1 and 2, respectively.
(d) Yield: 76 and 40% from **8c** using methods 1 and 2, respectively.
(e) Yield: 25% from **3a** using method 1.

3.7.2. 5-Methoxy-2-phenylbenzoxazole (2b). Yield: 80, 81 and 83% from **1b** using methods 1, 2 and 3, respectively. Mp 82–84 °C (ethanol); (Found: C, 74.58; H, 4.87; N, 6.05%. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22%.) ν_{max}/cm^{-1} 2361, 1479; δ_H 3.85 (3H, s, OCH_3), 6.94 (1H, dd, *J* 8.8 and 3.1, 6-H), 7.41 (1H, d, *J* 3.0, 4-H), 7.48 (4H, m, 3′,4′,5′-H and 7-H), 8.21 (2H, m, 2′,6′-H); δ_C 55.9, 102.9, 110.7, 113.7, 127.3, 127.5, 128.9, 131.4, 142.9, 145.4, 157.4, 163.8.

3.7.3. 5,6-Dimethoxy-2-phenylbenzoxazole (2c). Yield: 39, 42 and 51% from **1c** using methods 1, 2 and 3, respectively. Mp 114–115 °C (ethanol); (Found: C, 70.73; H, 5.24; N, 5.32%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%.) ν_{max}/cm^{-1} 3001, 1617; δ_H 3.95 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 7.14 (1H, s, 4-H), 7.26 (1H, s, 7-H), 7.48 (3H, m, 3′,4′,5′-H), 8.19 (2H, m, 2′,6′-H); δ_C 56.4, 56.5, 94.3, 101.8, 127.0, 127.5, 128.9, 130.9, 134.9, 145.1, 147.8, 148.4, 162.3.

3.7.4. 5-Methoxy-2-phenylbenzothiazole (10a).[10] Yield: 67 and 56% from **9a** using methods 1 and 2, respectively.

3.7.5. 6-Methoxy-2-phenylbenzothiazole (10b).[2] Yield: 27 and 70% from **9b** using methods 1 and 2, respectively.

3.7.6. 5,6-Dimethoxy-2-phenylbenzothiazole (10c).[2] Yield: 87, 73 and 84% from **9c** using methods 1, 2 and 3, respectively.

Acknowledgements

We gratefully acknowledge the support of NDR from UWI and thank Professor Vernon Box (CUNY) for useful discussions.

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