Preparation of 5-Bromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazol-2-ylamines

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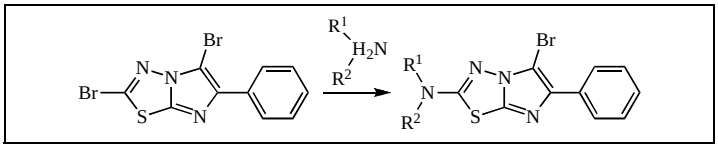

The reaction of primary or secondary amines with 2,5-dibromo-6-phenylimidazo[2,1-*b*][1,3,4]-thiadiazole (**5**) leads to a chemoselective replacement of the 2-Br substituent. The process represents a convenient route to the corresponding 2-ylamines **7a-d**. Hydrazine reacts in an analogous fashion (**5** → **7e**). The structure determinations are based on an X-ray crystal structure analysis and on one- and two-dimensional NMR measurements.

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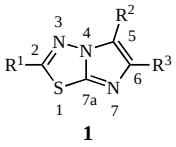
INTRODUCTION

During recent years there have been intense investigations on imidazo[2,1-*b*][1,3,4]thiadiazoles, since many of which are known to possess interesting pharmacological and/or biological properties such as antimicrobial [1-5], antitubercular [6,7], antiinflammatory [8-10], anticonvulsive [11,12], antihypertensive [13,14], anticancer [15-17] and antisecretory [18] activities. Many compounds of structure **1** with different substituents R^i (i = 1,2,3) are already known (Scheme 1). Nevertheless, there is a strong need to synthesize new derivatives in order to optimize their applications. Thus, several new synthetic strategies appeared in the literature [19-23].

Scheme 1



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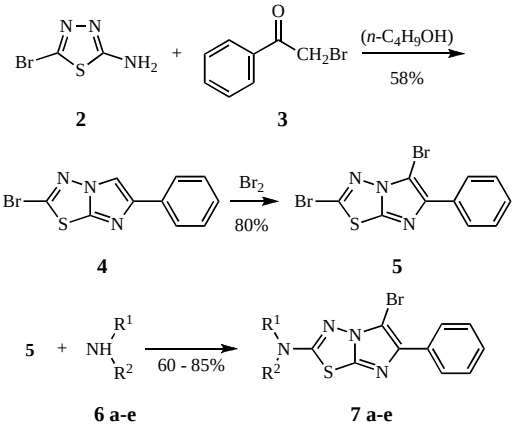
R^1, R^2, R^3: H, alkyl, aryl, hetaryl, amino, sulfonyl, halogen

We report here on the preparation of 2,5-dibromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazole and its selective substitution of the 2-Br group by the reaction with primary and secondary amines or hydrazine.

RESULTS AND DISCUSSION

The synthesis of 2-bromo-6-phenylimidazo[2,1-*b*]-[1,3,4]thiadiazole (**4**) was carried out by the condensation of 5-bromo-1,3,4-thiadiazol-2-ylamine (**2**) with α-bromoacetophenone (**3**) in boiling *n*-butanol (Scheme 2) [24]. The initially formed 2-imino-1,3,4-thiadiazole underwent a spontaneous ring closure and HBr elimination under these conditions. The reaction of **4** with bromine yielded in acetic acid in the presence of NaOAc the dibromo compound **5**. Treatment of **5** with primary or secondary amines **6a**-**d** afforded the imidazo[2,1-*b*][1,3,4]thiadiazol-2-ylamines **7a**-**d**. Hydrazine (**6e**) furnished **7e** in an analogous process. The nucleophilic replacement of the bromo substituent in 2-position is highly chemoselective. Even excess amounts of **6a**-**e** do not provoke an attack on C-5.

Scheme 2



7	R^1	R^2	Yield [%]	m.p. [°C]
a	H	CH_3	78	186
b	CH_3	CH_3	68	174
c	——— $(CH_2)_5$ ———		60	156
d	– $(CH_2)_2$ – O – $(CH_2)_2$ –		60	173
e	H	NH_2	85	188

The structure determination of **4** was confirmed by a crystal structure analysis. The target compounds **7a-e** were characterized by their ^1H and ^{13}C NMR spectra.

Figure 1 shows an PLATON plot of **4**. The benzene ring and the heterocyclic ring are almost coplanar as the torsion angle C(2)-C(1)-C(9)-C(14) of –12.8° reveals.

Table 1

Bond lengths, selected bond angles and torsion angles of 2-bromo-6-phenylimidazo[2,1-b][1,3,4]thiadiazole (**4**) (the numbering corresponds to Figure 1 and not to the nomenclature).

Bond lengths [Å]		Bond angles [°]	
S(6)—C(5)	1.743(4)	C(7)—S(6)—C(5)	87.0(2)
S(6)—C(7)	1.741(4)	S(6)—C(5)—N(4)	118.4(3)
C(5)—Br(1)	1.860(4)	C(5)—N(4)—N(3)	107.3(3)
C(5)—N(4)	1.274(5)	N(4)—N(3)—C(2)	133.9(3)
N(4)—N(3)	1.362(4)	N(3)—C(2)—C(1)	104.4(3)
N(3)—C(7)	1.356(5)	C(2)—C(1)—N(8)	111.7(3)
N(3)—C(2)	1.371(5)	C(1)—N(8)—C(7)	103.5(3)
C(2)—C(1)	1.372(5)	N(8)—C(7)—S(6)	138.5(3)
C(1)—N(8)	1.381(5)	C(2)—C(1)—C(9)	127.4(3)
N(8)—C(7)	1.307(5)	Torsion angles [°]	
C(1)—C(9)	1.474(5)	C(7)—N(3)—N(4)—C(5)	–0.8(5)
C(9)—C(10)	1.389(6)	C(2)—N(3)—N(4)—C(5)	–179.3(4)
C(10)—C(11)	1.380(6)	C(7)—N(3)—C(2)—C(1)	0.3(4)
C(11)—C(12)	1.362(6)	N(4)—N(3)—C(2)—C(1)	178.9(4)
C(12)—C(13)	1.371(6)	C(5)—S(6)—C(7)—N(8)	179.7(5)
C(13)—C(14)	1.386(5)	C(1)—N(8)—C(7)—S(6)	–178.5(4)
C(14)—C(9)	1.382(5)	C(2)—C(1)—C(9)—C(14)	–12.8(6)
		N(8)—C(1)—C(9)—C(10)	–14.5(5)

Table 2

^{1}H NMR data of the heterobicycles **4,5** and **7a-e** (δ values in $CDCl_3$, TMS as internal standard).

Comp.	2-NR^{1}R^2	5-H	6-Phenyl		
		(s)	*o*-H(m)	*m*-H(m)	*p*-H(m)
4		8.00	7.78	7.40	7.29
5			7.98	7.43	7.34
7a	2.49 (br, s, NH)		7.86	7.39	7.26
	2.89 (d, ^3J = 4.8 Hz, CH_3)				
7b	3.09 (s, CH_3)		7.97	7.39	7.27
7c	1.67 (m, 6 H, CH_2)		7.97	7.39	7.27
	3.45 (m, 4 H, NCH_2)				
7d	3.46 (m, 4 H, NCH_2)		7.96	7.40	7.28
	3.80 (m, 4 H, OCH_2)				
7e[a]	9.43 (br, s, NH)		7.90	7.41	7.26
	5.30 (br, s, NH_2)				

[a] Measurement in CD_3SOCD_3

Selected bond lengths, bond angles and torsion angles are listed in Table 1.

The ^{1}H and ^{13}C NMR data of **4,5** and **7a-e** are summarized in the Tables 2 and 3.

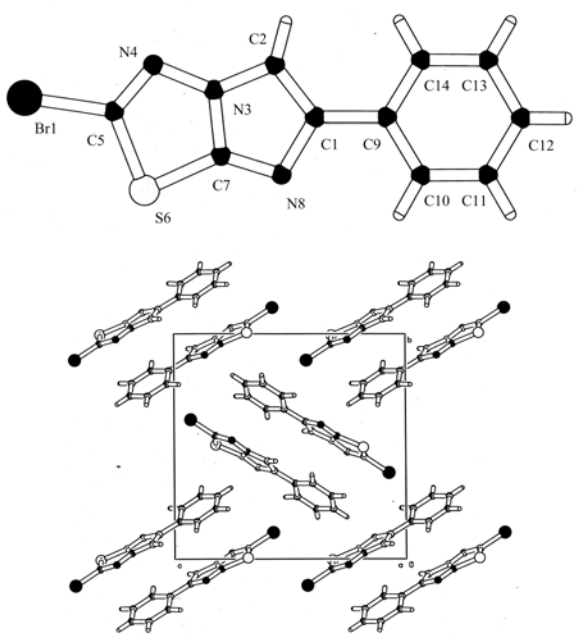


Figure 1: Upper part: PLATON plot of the crystal structure of 2-bromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazole (**4**) (the numbering corresponds to Table 1 and not to the nomenclature). Lower part: Elementary cell.

The chemoselectivity of the Br/NR^{1}R^2 replacement is documented by the ^{13}C NMR data. The high field shift of C-5, caused by the bromo substituents, is preserved on going from **5** to **7a-e**, whereas δ (C-2) shows a low-field shift of more than 30 ppm, when an N atom is attached. The assignment of the ^{1}H and ^{13}C signals (Tables 2 and 3) was based on 2D measurements (HMQC and HMBC).

Treatment of **7a** with acetic anhydride (**8**) yielded the acetamide **9a** (Scheme 3), which has a very low solubility in normal organic solvents.

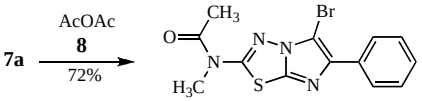
Table 3

^{13}C NMR data of the heterobicycles **4,5** and **7a-e** (δ values in $CDCl_3$, TMS as internal standard).

Comp.	Heterobicyclic scaffold			6-Phenyl				2-NR^{1}R^2
	C-2	C-5	C-6 / C-7a	*i*-C	*o*-C	*m*-C	*p*-C	CH_3 / CH_2
4	133.1	109.8	145.5 / 146.0	133.1	125.1	128.8	128.0	
5	132.4	93.4	142.6 / 144.4	133.6	126.8	128.6	128.2	
7a[a]	162.8	91.9	138.3 / 139.8	133.4	125.7	128.6	127.2	30.5
7b	164.2	91.9	139.4 / 140.4	133.6	126.3	128.3	127.2	40.0
7c	164.5	92.0	139.5 / 140.2	135.6	126.3	128.3	127.1	49.5 (NCH_2)
								24.9 (CH_2)
								23.8 (CH_2)
7d	164.6	92.3	139.9 / 139.9	133.4	126.3	128.4	127.3	65.8 (OCH_2)
								48.3 (NH_2)
7e[a]	177.3	91.1	137.8 / 140.7	133.6	125.7	128.5	127.1	

[a] Measurement in CD_3SOCD_3

Scheme 3



9a m.p. 245 °C

Imidazo[2,1-*b*][1,3,4]thiadiazol-2-ylamines can be easily prepared by nucleophilic substitution reactions of the 2-Br derivative and primary and secondary amines (or hydrazine). The 5-Br group does not disturb this chemoselective process because it does not show any reactivity toward amines. Obviously the 1,3,4-thiadiazole ring is much more prone to this type of replacement reaction than the imidazole ring.

EXPERIMENTAL

Melting points were determined on a Boetius apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with the Bruker machines AM 400 and AMX 400 using $CDCl_3$ or CD_3SOCD_3 as solvent and TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 95 applying the field desorption (FD) technique.

5-Bromo-1,3,4-thiadiazol-2-ylamine (**2**) was generated according to reference [25,26].

2-Bromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazole (4). 1.80 g (10.0 mmol) of **2** and 1.99 g (10.0 mmol) of α-bromoacetophenone [27] were refluxed in 50 mL of *n*-butanol for 8 h. The reaction mixture was cooled to 20 °C, the formed precipitate filtered and washed three times with 7 mL H_2O each. Recrystallization from 1,4-dioxane/$CHCl_3$ (5:1) gave 1.62 g (58%) crystals which melted at 195 °C. FD MS: *m/z* (%) = 281 (100) [M^+, Br isotope pattern]. *Anal.* Calcd. for $C_{10}H_6BrN_3S$ (280.2): C, 42.87; H, 2.16; N, 15.00; S, 11.45. Found: C, 42.65; H, 2.05; N, 15.15; S, 11.32.

2,5-Dibromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazole (5). To 2.80 g (10.0 mmol) **4** dissolved in 30 mL acetic acid, 1.59 g (10.0 mmol) Br_2, dissolved in 3 mL acetic acid, was dropped at ambient temperature within 15 min. The reaction was vigorously stirred for 75 min. A saturated aqueous solution of 0.82 g (10.0 mmol) NaOAc was slowly added under cooling. The formed precipitate was collected by filtration and washed with H_2O (4 x 15 mL). Recrystallization from 1,4-dioxane yielded 2.87 g (80%) **5** which melted at 132 °C. FD MS: *m/z* (%) = 359 (100) [M^+, Br_2 isotope pattern]. *Anal.* Calcd. for $C_{10}H_5Br_2N_3S$ (359.1): C, 33.45; H, 1.40; N, 11.70; S, 8.93. Found: C, 33.25; H, 1.32; N, 11.85; S, 9.05.

(5-Bromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazol-2-yl)-methylamine (7a). Compound **5** (3.59 g, 10.0 mmol, in 28 mL CH_3OH) and an aqueous solution of methylamine (**6a**) (0.62 g, 20.0 mmol, in 1.86 g H_2O) was refluxed for 3 h. After evaporation of the volatile parts, the residue was suspended in 4 mL H_2O and extracted with $CHCl_3$ (3 x 30 mL). The organic phase was dried over Na_2SO_4 and evaporated. Crystallization of the residue from 1,4-dioxane/$CHCl_3$ (10:1) afforded 2.41 g (78%) **7a** which melted at 186 °C. FD MS: *m/z* (%) = 310 (100) [M^+, Br pattern]. *Anal.* Calcd. for $C_{11}H_9BrN_4S$ (309.2): C, 42.73; H, 2.93; N, 18.12; S, 10.37. Found: C, 42.61; H, 2.77; N, 18.21; S, 10.35.

(5-Bromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazol-2-yl)-dimethylamine (7b). Compound **5** (3.59 g, 10.0 mmol) and an aqueous solution of dimethylamine (**6b**) (1.80 g, 40 mmol) were refluxed in 15 mL 1,4-dioxane/CH_3OH (1:1) for 2 h. Work-up, as described for **7a**, and crystallization from 1,4-dioxane/$CHCl_3$ (5:1) yielded 2.20 g (68%) **7b** which melted at 174 °C. FD MS: *m/z* (%) = 324 (100) [M^+, Br pattern]. *Anal.* Calcd. for $C_{12}H_{11}BrN_4S$ (323.2): C, 44.59; H, 3.43; N, 17.33; S, 9.92. Found: C, 44.69; H, 3.45; N, 17.23; S, 9.81.

5-Bromo-6-phenyl-2-piperidin-1-ylimidazo[2,1-*b*][1,3,4]-thiadiazole (7c). Compound **5** (3.59 g, 10.0 mmol) and 1.70 g (20.0 mmol) piperidine (**6c**) were refluxed in 30 mL isopropanol for 3 h. Work-up and recrystallization as described for **7b** yielded 2.18 g (60%) **7c** which melted at 156 °C. FD MS: *m/z* (%) = 364 (100) [M^+, Br isotope pattern]. *Anal.* Calcd. for $C_{15}H_{15}BrN_4S$ (363.3): C, 49.59; H, 4.16; N, 15.42; S, 8.83. Found: C, 49.38; H, 4.25; N, 15.61; S, 8.68.

5-Bromo-2-morpholin-4-yl-6-phenylimidazo[2,1-*b*][1,3,4]-thiadiazole (7d). The reaction of 3.59 g (10.0 mmol) **5** and 1.74 g (20.0 mmol) morpholine (**6d**) was carried out as described for **7c**. The residue, obtained after the evaporation of the volatile parts, was dissolved in $CHCl_3$, extracted with 15 mL 1% HCl and 2 x 15 mL H_2O. The organic layer was dried with $CaCl_2$ and concentrated. Crystallization from $CHCl_3$ yielded 2.20 g (60%) **7d** which melted at 173 °C. FD MS: *m/z* (%) = 366 (100) [M^+, Br isotope pattern]. *Anal.* Calcd. for $C_{14}H_{13}BrN_4OS$ (365.3): C, 46.04; H, 3.59; N, 15.34; S, 8.78. Found: C, 46.12; H, 3.45; N, 15.39; S, 8.71.

(5-Bromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazol-2-yl)-hydrazine (7e). To 3.59 g (10.0 mmol) **5**, dissolved in 20 mL EtOH/DMF (5:1), 0.75 g (15.0 mmol) hydrazine hydrate was added dropwise under stirring within 20 min. After further 40 min. at room temperature, the generated precipitate was filtered, washed with water (3 x 15 mL) and recrystallized from EtOAc/1,4-dioxane (10:3). Yield 2.64 g (85%), m.p. 187 °C. FD MS: *m/z* (%) = 311 (100) [M^+, Br isotope pattern]. *Anal.* Calcd. for $C_{10}H_8BrN_5S$ (310.2): C, 38.72; H, 2.60; N, 22.58; S, 10.34. Found: C, 38.59; H, 2.45; N, 22.43; S, 10.27.

***N*-(5-Bromo-6-phenylimidazo[2,1-*b*][1,3,4]thiadiazol-2-yl)-*N*-methylacetamide (9a).** Compound **7a** (3.09 g, 10.0 mmol) was refluxed in 35 mL (38.04 g, 373.0 mmol) acetic anhydride (**8**) for 1 h. The formed precipitate was filtered, washed with H_2O (3 x 15 mL) and recrystallized from DMF. Yield 2.53 g (72%), m.p. 245 °C. FD MS: *m/z* (%) = 352 (100) [M^+, Br isotope pattern]. ^{1}H NMR (CD_3SOCD_3): δ = 2.44 (s, 3 H, CH_3), 3.63 (s, 3 H, NCH_3), 7.33 (m, 1 H, *p*-H, phenyl), 7.46 (m, 2 H, *m*-H, phenyl), 7.95 (m, 2 H, *o*-H, phenyl). ^{13}C NMR (CD_3SOCD_3): δ = 22.8 (CH_3), 35.5 (NCH_3), 91.8 (C-5), 126.2 (*o*-CH, phenyl), 127.7 (*p*-CH, phenyl), 128.7 (*m*-CH, phenyl), 132.8 (*i*-C, phenyl), 172.3 (CO); the solubility of **9a** is so low that the signals of the remaining quaternary carbon atoms C-2, C-6 and C-7a are not clearly visible within the level of the electronic noise. *Anal.* Calcd. for $C_{13}H_{11}BrN_4OS$ (351.2): C, 44.46; H, 3.16; N, 15.95; S, 9.13. Found: C, 44.34; H, 2.95; N, 15.86; S, 9.05.

Crystal structure analysis of compound 4. Structure solution, refinement and data output were carried out with SHELX-97 program package [28]. H atoms were placed in geometrically calculated positions using a riding model. Details of the X-ray crystal structure analysis are summarized in Table 4.

Crystallographic data for **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary

publication no. CCDC 637 337. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

Table 4

Details of X-ray crystal structure analysis of **4**

Formula	$C_{10}H_6N_3SBr$
M_r [g mol^{-1}]	280.15
Crystal size [mm^3]	0.1 x 0.2 x 0.3
Space group	P 2_1 / n (monoclinic)
Cell constants	
a [Å]	5.561(2)
b [Å]	13.400(5)
c [Å]	13.891(5)
β [°]	83.87(1)
V [Å^3]	1029.3(10)
Z	4
D_x [Mgm^{-3}]	1.808
Diffractometer	Smart CCD
Radiation	Mo–K$_\alpha$ (λ = 0.71073 Å), graphite monochromator
Scan type	CCD
Scan width [°]	0.3
Range [°]	$2 \le \Theta \le 29$
	$-6 \le h \le 7, -17 \le k \le 17, -18 \le l \le 18$
F (000)	552
T [°C]	25
No. of refl. measured	13880
indep.	2626
observed	1705 (/ $\sigma(F) > 4.0$
R_σ	0.0773

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