A Facile One Pot Synthesis of 1-Alkylbenzimidazoline-2-thiones

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Reactions of benzimidazoline-2-thione with alkyl halides in the presence of sodium naphthalenide in tetrahydrofuran at room temperature under a nitrogen atmosphere afforded 1-alkyl-2-alkylthiobenzimidazoles in excellent yields, which underwent a bond cleavage between S and C of alkyl group to give excellent yields of 1-alkylbenzimidazoline-2-thiones by the treatment with an additional amount of sodium naphthalenide.

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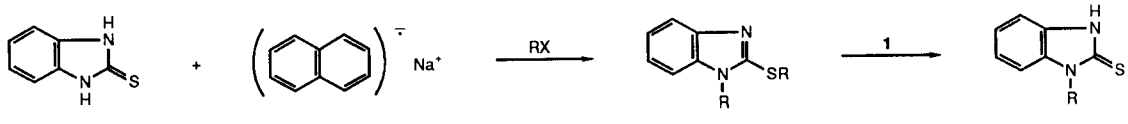
It has been well known that sodium naphthalenide (**1**) acts as not only a strong base but also a good electron donor [1]. Although there are ample reports demonstrating such properties of **1**, there appears to be no example in which both properties of **1** are utilized in one pot synthesis. We undertook the synthesis of 1-alkylbenzimidazoline-2-thiones as a model case for the application of the idea because only a few methods to prepare 1-alkylbenzimidazoline-2-thiones have been reported. For the most part only two methods have been used: the first one consists of the cyclization of *N*-alkylphenylenediamines in carbon disulfide at the reflux temperature, giving 60 to 76% yields [2-8]. However, in order to utilize this method, the *N*-alkylphenylenediamines need to be synthesized. The second method [9-10] is to first synthesize 2-alkylthiobenzimidazole methiodides from the reaction of 2-alkylthiobenzimidazoles with methyl iodide in methanol under reflux for over 48 hours, followed by refluxing of the resulting iodide salts with pyridine for 1 hour to give the desired compounds in about 60% yields.

Among the others which appear to be used in limited cases are the following: 1-methylbenzimidazole reacted with sulfur at 268° to give 1-methylbenzimidazoline-2-thione [11]. 1-Methyl-2-chlorobenzimidazole reacted with either sodium hydrogen sulfide or thiourea in hydroxide solution to give 1-methylbenzimidazoline-2-thione [12]. 1-(2-Carbomethoxy-1-propyl)benzimidazoline-2-thione [13] was directly synthesized in 18% yield from the reaction of benzimidazoline-2-thione (**2**) with methyl methacrylate in dimethylformamide containing sodium carbonate for 6 hours. 1-Allylbenzimidazoline-2-thione was prepared in 50% yield by Claisen type rearrangement of 2-allylthiobenzimidazole [13].

Compound **2** was readily dissolved in dried tetrahydrofuran and was dialkylated on S and N atoms in excellent yields by the addition of **1** in tetrahydrofuran until the green color of **1** persisted for a few seconds, followed by the addition of excess amount of primary alkyl halides (Table I).

TABLE I

Yields of 1-Alkyl-2-alkylthiobenzimidazoles **3a-3f** and 1-Alkylbenzimidazoline-2-thiones **4a-4f**



2 **1** **3** **4**

RX	Stirring time, hours (2 → 3)	3	R	3 %	4 %
MeI	3	**a**,	Me	97	88 (87)
EtI	5	**b**,	Et	100	94 (94)
PrI	7	**c**,	Pr	100	93 (90)
i-PrBr [a]	20 days	**d**,	*i*-Pr	33	
CH_2=$CHCH_2Br$	5	**e**,	CH_2=$CHCH_2$	100	92 (91)
$PhCH_2Br$	3	**f**,	$PhCH_2$	100	93 (90)

Numbers in the parenthesis represent the isolated yields from successive treatments without isolation of **3**. Attempts for the preparation of **4d** was not made. [a] In addition to 33% of **3d**, 50% of 2-isopropylthiobenzimidazole and 12 % of **2** were obtained.

Since the anion radical of an alkyl aryl sulfide is rapidly cleaved to form an alkyl radical and an arenethiolate [14-17], **1** in tetrahydrofuran was rapidly added to **3** in tetrahydrofuran under a nitrogen atmosphere to generate anion radicals of **3** by an electron transfer. An electron transfer from **1** to **3** was monitored by the disappearance of the green color of **1**. From these reactions compounds **4** were obtained in excellent yields as shown in Table I.

The formation of **4** in these reactions can be explained by a bond cleavage between S and C of an alkyl group of **5**.

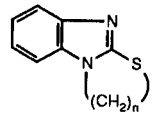
Scheme 1

5

4

Compounds **4** could also be obtained in excellent yields in one pot without the isolation of **3** by carrying out successively two processes, *i.e.* dialkylation on S and N of **2**, followed by bond cleavage between S and C of an alkyl group with **1**.

In order to detect radical species formed from **5**, compounds **6a** and **6b** were synthesized in 88% and 85% yields using 1,3-dibromopropane and 1,4-dibromobutane, respectively in the presence of solid sodium hydroxide in tetrahydrofuran. These compounds were treated with **1**, yielding **4c** and 1-butylbenzimidazoline-2-thione (**7**), respectively. The variation of yields of **4c** and **7** was also



6a, n = 3
6b, n = 4

investigated under the conditions where **1** was added to **6a** and **6b** in tetrahydrofuran containing toluene and cumene, respectively. Table II lists the percent yield data for the isolated products.

Table II

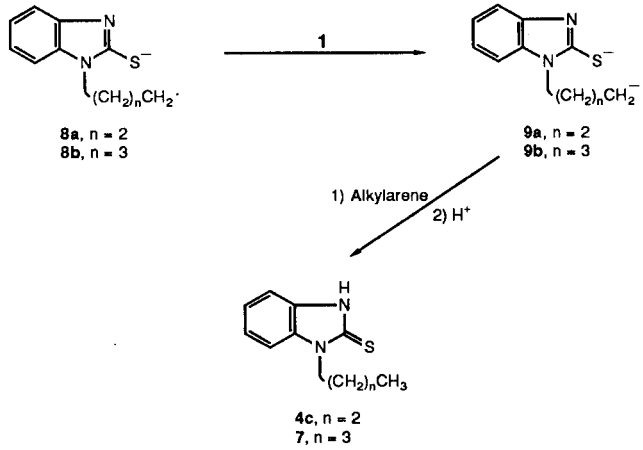
Percent Yields of **4c** and **7** in Different Solvents

	THF [a]	THF + Toluene	THF + Cumene
4c	51	67	49
7	47	65	50

[a] Tetrahydrofuran.

The yields of **4c** and **7** increased to 67% and 65% respectively in tetrahydrofuran containing toluene but was not essentially changed in tetrahydrofuran containing cumene. These results can be accounted for by a proton transfer from alkylarenes to alkyl carbanions **9a** and **9b**, which are generated by an electron transfer from **1** to anion radicals **8a** and **8b** (Scheme 2) because the rate of electron transfer between **1** and the alkyl radical is virtually diffusion controlled [18-19] and toluene acts as a better proton donor than cumene [20].

Scheme 2

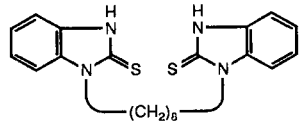


8a, n = 2
8b, n = 3

9a, n = 2
9b, n = 3

4c, n = 2
7, n = 3

The involvement of a hydrogen atom transfer from alkylarenes to **8a** and **8b** is less likely because higher yields of **4c** and **7** are expected in the presence of cumene, being a better hydrogen atom donor compared with toluene [21]. In addition, bibenzyl and acetophenone, which are radical derived products from toluene and cumene, respectively were not detected. However, isolation of **10** in 6% yield along with 65% of **7** in the presence of toluene support the initial formation of anion radical with a radical center on carbon, **8b**, rather than anion radical with a radical center on sulfur.



10

EXPERIMENTAL

Benzimidazoline-2-thione (**2**), naphthalene, and all alkyl halides used were obtained from Aldrich-Chemie, Germany. Tetrahydrofuran was dried over calcium hydride. Column chromatography was performed using silica gel (Merck, 70-230 mesh, ASTM). The ^{1}H nmr spectra were recorded on a Varian EM-360 A 60 MHz spectrometer using tetramethylsilane as an internal standard and solvents were specified in each case. Mass spectra were obtained using a Hewlett Packard 5985 B mass

Table III

Physical and Spectroscopic Data of 1-Alkyl-2-alkylthiobenzimidazoles

Compound number	Molecular formula	^{1}H NMR (deuteriochloroform) δ	Analysis (%) Calcd./Found C	H	N	MS m/z (M$^+$)
3a [a]	$C_9H_{10}N_2S$	2.77 (s, 3H, CH_3S), 3.57 (s, 3H, CH_2N), 7.07-7.20 (m, 3H, H of positions 5, 6, 7), 7.47-7.70 (m, 1H, H of position 4)	60.64 60.48	5.65 5.63	15.72 15.69	178
3b	$C_{11}H_{14}N_2S$	1.23-1.63 (m, 6H, $2CH_3$), 3.49 (q, 2H, J = 8 Hz, CH_2S), 4.17 (q, 2H, J = 8 Hz, CH_2N), 7.21-7.33 (m, 3H, H of positions 5, 6, 7), 7.57-7.95 (m, 1H, H of position 4)	64.04 64.16	6.84 6.83	13.58 13.39	206
3c	$C_{13}H_{18}N_2S$	0.86-1.22 (m, 6H, $2CH_3$), 1.49-2.15 (m, 4H, $2CH_2$), 3.36 (t, 2H, J = 7 Hz, CH_2S), 3.99 (t, 2H, J = 7 Hz, CH_2N), 7.10-7.29 (m, 3H, H of positions 5, 6, 7), 7.54-7.81 (m, 1H, H of position 4)	66.64 66.58	7.74 7.59	11.95 11.76	234
3d	$C_{13}H_{18}N_2S$	1.55 (t, 12H, $4CH_3$), 4.17 (quintet, 1H, J = 7 Hz, CH_2S), 4.70 (quintet, 1H, J = 7 Hz, CHN), 7.07-7.84 (m, 4H, ArH)	66.64 66.61	7.74 7.67	11.95 11.83	234
3e	$C_{13}H_{14}N_2S$	3.90-4.11 (m, 2H, CH_2S), 4.51-4.73 (m, 2H, CH_2N), 4.78-5.45 (m, 4H, $2CH_2=$), 5.54-6.27 (m, 2H, 2-CH=), 7.06-7.30 (m, 3H, H of positions 5, 6, 7), 7.53-7.79 (m, 1H, H of position 4)	67.79 67.74	6.13 6.05	12.16 12.09	230
3f [b]	$C_{21}H_{18}N_2S$	4.64 (s, 2H, CH_2S), 5.19 (s, 2H, CH_2N), 6.97-7.50 (m, 13H, H of positions 5, 6, 7 and phenyl), 7.60-7.89 (m, 1H, H of position 4)	76.33 76.17	5.49 5.33	8.48 8.28	330

[a] mp 58-59°, recrystallized from *n*-hexane, lit [22] mp 50-52°. [b] mp 93-93.5°, recrystallized from ethanol, lit [13] mp 116-117°. All other compounds were obtained as liquids.

Table IV

Physical and Spectroscopic Data of 1-Alkylbenzimidazoline-2-thiones

Compound number	^{1}H NMR (deuteriochloroform) δ	mp (°C) Solvent	Lit	MS m/z (M$^+$)
4a	3.80 (s, 3H, CH_3N), 7.05-7.33 (m, 4H, ArH), 11.70 (s, 1H, NH)	192 benzene	191 [7]	164
4b	1.43 (t, 3H, J = 7 Hz, CH_3), 4.44 (q, 2H, J = 7 Hz, CH_2N), 7.15-7.44 (m, 4H, ArH), 11.80 (s, 1H, NH)	163-164 *n*-hexane-benzene (v:v, 2:1)	163-164 [9]	178
4c	1.03 (t, 3H, J = 6 Hz, CH_3), 1.92-2.30 (m, 2H, CH_2), 4.28 (t, 2H, J = 8 Hz, CH_2N), 7.04-7.43 (m, 4H, ArH), 12.08 (s, 1H, NH)	113-113.5 *n*-hexane	109-111 [9]	192
4e	4.89-5.14 (m, 2H, CH_2N), 5.16-5.45 (m, 2H, $CH_2=$), 5.64-6.30 (m, 1H, -CH=), 7.09-7.41 (m, 4H, ArH), 11.77 (s, 1H, NH)	111.5-112 *n*-hexane	115-117 [13]	190
4f [a]	5.56 (s, 2H, CH_2N), 7.00-7.50 (m, 9H, ArH), 11.88 (s, 1H, NH)	186-187 ethanol		240

[a] *Anal.* Calcd. for $C_{14}H_{12}N_2S$: C, 70.00; H, 5.03; N, 11.66. Found: C, 69.81; H, 4.98; N, 11.62.

spectrometer. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Microanalysis were performed by Korea Research Institute of Chemical Technology, Dae Jeon, Korea.

Sodium Naphthalenide (**1**).

A solution of naphthalene (2.00 g, 15.6 mmoles) and sodium turnings (1.0 g) in tetrahydrofuran (60 ml) was stirred for 3 hours at room temperature under nitrogen atmosphere after the appearance of a green color. This solution was added to the solution of **3** by a cannula. The concentration of **1** was calculated by quantifying 1,4-dihydronaphthalene formed by quenching the anion radical with water after 3 hours stirring by ^{1}H nmr spectroscopy and it was 0.189 *M*.

General Procedure for the Preparation of 1-Alkyl-2-alkylthiobenzimidazoles **3a-3f**.

To a solution of **2** (0.60 g, 3.99 mmoles) in tetrahydrofuran (20 ml) was added **1** in tetrahydrofuran until the green color of **1** persisted for about 10 seconds, followed by the addition of alkyl halide (15-19 mmoles). The mixture was stirred for 5-7 hours, followed by removal of the solvent on a rotary evaporator. Water (30 ml) was added to the residue and then the mixture was extracted with chloroform. The combined chloroform extracts were dried on magnesium sulfate and the solvent was evaporated to dryness. The residue was chromatographed on silica gel column (2 x 12 cm). Elution with *n*-hexane (150 ml) gave a mixture of naphthalene and 1,4-dihydronaphthalene. Elution next with

chloroform (200 ml) afforded **3a-3f** (Table III).

1-Isopropyl-2-isopropylthiobenzimidazole (**3d**).

Compound **3d** was prepared according to the general procedure described above except the following: The reaction mixture was stirred for 20 days. Extraction was performed with a mixture of chloroform and ethyl acetate (v:v, 1:1, 100 ml). After naphthalene and 1,4-dihydronaphthalene were eluted with *n*-hexane, **3d** was eluted with a mixture of *n*-hexane and ethyl acetate (v:v, 4:1), yielding 0.15 g (0.65 mmoles, 33%) of **3d** (see Table III for the spectroscopic data). Continuous elution with a mixture of *n*-hexane and ethyl acetate (v:v, 3:1) afforded 2-isopropylthiobenzimidazole (0.19 g, 0.99 mmole, 50%), recrystallized from ethanol, mp 186-187°; ^{1}H nmr (DMSO-d_6 + deuteriochloroform, v:v, 1:7): δ 1.47 (d, 6H, J = 7 Hz, $2CH_3$), 4.09 (quintet, 1H, J = 7 Hz, CHS), 7.11-7.70 (m, 4H, ArH), 10.4 (s, 1H, NH); ms: m/z 192 (M^+).

Anal. Calcd. for ($C_{10}H_{12}N_2S$): C, 62.47; H, 6.29; N, 14.57. Found: C, 62.53; H, 6.27; N, 14.39.

Finally elution with a mixture of *n*-hexane and ethyl acetate (v:v, 1:1) afforded **2** (0.04 g, 0.24 mmoles, 12%).

General Procedure for the Preparation of 1-Alkylbenzimidazoline-2-thiones **4a-4f** from **3a-3f**.

To a solution of **3a-3f** (2-3 mmoles) in tetrahydrofuran (20 ml) was rapidly added **1** in tetrahydrofuran until the green color of **1** in tetrahydrofuran persisted. Then the mixture was immediately quenched with water (20 ml). After tetrahydrofuran was removed the residue was extracted with chloroform, which was dried over magnesium sulfate. The residue after the solvent was removed was chromatographed on a silica gel column (2 x 15 cm). Naphthalene was eluted with *n*-hexane (80 ml) and elution next with chloroform (150 ml) afforded **4a-4f** (Table IV).

2,3,4-Trihydro-1,3-thiazino[3,2-*a*]benzimidazole (**6a**).

To a solution of **2** (2.00 g, 13.32 mmoles) in tetrahydrofuran (150 ml) were added solid sodium hydroxide (2.00 g, 50.00 mmoles) and 1,3-dibromopropane (2.70 g, 13.35 mmoles) over a period of 3 hours. The mixture was stirred overnight and water (100 ml) was added to the mixture. After tetrahydrofuran was evaporated, the aqueous solution was extracted with a mixture of chloroform (100 ml) and ethyl acetate (50 ml), which was dried on magnesium sulfate. After the solvent was evaporated, the residue was chromatographed on silica gel column (2 x 20 cm). Elution with 200 ml of a mixture of *n*-hexane and ethyl acetate (v:v, 2:1) gave 0.14 g of an unknown mixture and elution with 300 ml of a mixture of *n*-hexane and ethyl acetate (v:v, 1:1) gave a solid, recrystallized from a *n*-hexane:benzene mixture (v:v, 2:1) to give 2.23 g (11.72 mmoles, 88%) of **6a**, mp 141-142°; ^{1}H nmr (deuteriochloroform): δ 2.07-2.50 (m, 2H, CH_2), 2.91-3.20 (m, 2H, CH_2S), 3.97 (t, 2H, J = 6 Hz, CH_2N), 6.98-7.34 (m, 3H, H of positions 6, 7, 8), 7.43-7.80 (m, 1H, H of position 9); ms: m/z 190 (M^+).

Anal. Calcd. for ($C_{10}H_{10}N_2S$): C, 63.13; H, 5.30; N, 14.72. Found: C, 63.03; H, 5.25; N, 14.58.

2,3,4,5-Tetrahydro-1,3-thiazepino[3,2-*a*]benzimidazole (**6b**).

Compound **6b** was prepared by a procedure similar to that which afforded **6a**. The yield of **6b** was 85%, mp 133-134°, (lit [13] mp 133-134°); ^{1}H nmr (deuteriochloroform): δ 1.67-2.44 (m, 4H, CH_2CH_2), 2.70-3.00 (m, 2H, CH_2S), 4.17-4.45 (m, 2H, CH_2N), 7.10-7.38 (m, 3H, H of positions 7, 8, 9), 7.59-7.85 (m, 1H, H of position 10); ms: m/z 204 (M^+).

1-Propylbenzimidazoline-2-thione (**4c**) from **6a**.

To a solution of **6a** (1.04 g, 5.44 mmoles) in tetrahydrofuran (30 ml) was added **1** in tetrahydrofuran under a nitrogen atmosphere over the period of 2.5 hours. The mixture was quenched immediately with water when the green color of **1** persisted. The reaction mixture was worked up as described earlier and the residue was chromatographed on a silica gel column (2 x 20 cm). Naphthalene was removed by elution with *n*-hexane (120 ml). Elution with 100 ml of a mixture of *n*-hexane and ethyl acetate (v:v, 3:1) gave **4c** (0.54 g, 2.79 mmoles, 51%).

This reaction was carried out in tetrahydrofuran containing toluene. To a solution of **6a** (1.04 g, 5.44 mmoles) in a mixture of tetrahydrofuran (25 ml) and toluene (25 ml) was added **1** in tetrahydrofuran under a nitrogen atmosphere over the period of 2.5 hours. The mixture was worked up as before. The yield of **4c** was 0.70 g (3.65 mmoles, 67%).

When the reaction was carried out in tetrahydrofuran (25 ml) containing cumene (25 ml) using the same amount of **6a** as in the previous reaction, 0.51 g (2.65 mmoles, 49%) of **4c** was obtained.

1-Butylbenzimidazoline-2-thione (**7**) from **6b**.

Compound **7** was prepared from **6b** (0.95 g, 4.65 mmoles) by a procedure similar to that which afforded **4c** from **6a**. Naphthalene was removed by the elution with *n*-hexane (120 ml). Elution with 100 ml of a mixture of *n*-hexane and ethyl acetate (v:v, 4:1) gave **7**, which was recrystallized from *n*-hexane. The yield of **7** was 0.45 g (2.18 mmoles, 47%), mp 91-93°; ^{1}H nmr (deuteriochloroform): δ 0.98 (t, 3H, J = 7 Hz, CH_3), 1.15-2.10 (m, 4H, CH_2CH_2), 4.30 (t, 2H, J = 7 Hz, CH_2N), 7.04-7.34 (m, 4H, ArH), 12.14 (s, 1H, NH); ms: m/z 306 (M^+).

Anal. Calcd. for ($C_{11}H_{14}N_2S$): C, 64.06; H, 6.84; N, 13.58. Found: C, 64.17; H, 6.68; N, 13.62.

1,8-Bis(2-mercapto-1-benzimidazoyl)octane (**10**).

After **7** was eluted with a *n*-hexane-ethyl acetate mixture, elution with 60 ml of a mixture of *n*-hexane and ethyl acetate (v:v, 2:1) afforded 0.03 g (0.07 mmoles, 3%) of **10**, mp of crude compound, 219-223°; ^{1}H nmr (DMSO-d_6 + deuteriochloroform, v:v, 1:5): δ 1.15-2.13 (m, 12H, $6CH_2$), 4.29 (t, 4H, J = 7 Hz, $2CH_2N$), 7.05-7.35 (m, 8H, ArH), 12.35 (s, 2H, 2NH); ms: m/z 410 (M^+).

This reaction was run in tetrahydrofuran containing toluene. To a solution of **6b** (1.02 g, 4.97 mmoles) in a mixture of tetrahydrofuran (30 ml) and toluene (30 ml) was added **1** in tetrahydrofuran as above. The mixture was worked up as in the previous reaction. From this reaction were obtained **7** (0.67 g, 3.25 mmoles, 65%) and **10** (0.06 g, 0.16 mmoles, 6%).

When the reaction was carried out in tetrahydrofuran (25 ml) containing cumene (25 ml) using the same amount of **6b** (1.02 g) as in the previous reaction, 0.51 g (2.49 mmoles, 50%) of **7** and 0.08 g (0.19 mmoles, 8%) of **10** were obtained.

General Procedure for the Preparation of **4a-4f** from **2**.

Compounds **3a-3f** were prepared according to the general procedure described earlier. Without the isolation of **3a-3f**, **1** in tetrahydrofuran was added to the reaction mixture being stirred for 5 minutes under nitrogen atmosphere until green color of **1** persisted. The mixture was worked up as usual. Elution with *n*-hexane afforded a mixture of naphthalene, 1,4- and 1,2-dihydronaphthalenes. Elution next with a mixture of *n*-hexane

and ethyl acetate (v:v, 4:1) afforded **4a-4f** (Table IV).

Acknowledgement.

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