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SULFUR-CONTAINING HETEROCYCLES DERIVED BY REACTION OF *N*-THIOACYLAMINO ALCOHOLS WITH LAWESSON'S REAGENT AND SAPONIFICATION OF *N*-THIOACYLAMINO ESTERS

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Abstract- The treatment of 2-*N*-thioacylamino alcohols (**1**) with Lawesson's reagent [**LR**: 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiaphosphetane 2,4-disulfide] afforded the sulfur-containing heterocycles, 1,3-thiazolines (**2**) in moderate to good yields, exclusively. The saponification of *N*-thioacylamino esters (**4**), which were prepared by the thionation of *N*-acylamino esters (**3**) with **LR**, with K_2CO_3 gave 3,1-benezothiazines (**5**) and 3,1-benzoxazines (**6**).

INTRODUCTION

The five- and six-membered sulfur-containing heterocycles such as thiazolines and thiazines are synthetically as well as biologically interesting compounds and a number of methods for the synthesis of these compounds have been reportrd.[1] 2,4-Bis(*p*-methoxyphenyl)-1,3,2,4-dithiaphosphetane 2,4-disulfide, commonly known as Lawesson's reagent (**LR**), is one of the best known thionation reagent, and its advantage has been demonstrated for thionation of a wide variety of carbonyl compounds.[2] **LR** is also utilized in the synthesis of five- and six-membered sulfur-[3] and phosphorus-containing heterocycles.[4] Recently, we have reported the direct conversion of alcohols into thiols by the treatment of alcohols with **LR**,[5] and also for the novel synthesis of sulfur-containing heterocycles[3e,3i-n] by treating bifunctional compounds possessing such as hydroxyl, carbonyl and amide groups with **LR**. For instance, thiazolines and benzothiazines were obtained from the reaction of 2-*N*-acylamino alcohols and [2-(*N*-acylamino)phenyl]alkanols with an equimolar amount of **LR**. [3e,i] It has been been suggested that initially produced respective thiols undergo further thionation of the amide carbonyl giving thioacylamino thiols, which subsequently cyclize with elimination of hydrogen sulfide to yield thiazolines and benzothiazines. Recently, Lellouche and his coworkers[6] have reported the novel synthesis of thiazolines from 2-*N*-

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Dedicated to Professor A. I. Meyers on the occasion of his 70th birthday.

thioacylamino alcohols and DAST (diethylamidosulfur fluoride), which is a powerful hydroxy activating reagent for the efficient cyclization. To extend the usage of **LR** to other multifunctional substrates, we have investigated the reaction of thioacylamino alcohols (**1**) and acylamino esters (**3**) with **LR**, and our results are described in this paper.

RESULTS AND DISCUSSION

1. *Reaction of 2-N-Thioacylamino alcohols* (**1**) *with* **LR**.

The reaction of 2-*N*-thioacylamino alcohols (**1**) with **LR** in toluene at reflux temperature under argon for 15 min yielded thiazolines (**2**) in moderate to good yields (Scheme 1 and Table 1). The yields of thiazolines (**2**) obtained in this reaction are rather higher than those obtained by the reaction of 2-*N*-acylamino alcohols with **LR**[2i] and by the reaction of **1** with DAST.[6] 2-*N*-Thioacylamino alcohol (**1f**) was recovered quantitatively when refluxed in toluene in the absence of **LR**. These results suggest that in the reaction of 2-*N*-thioacylamino alcohols (**1**) with **LR**, the hydroxy group is initially thionated and then followed by the cyclization and the elimination of H_2S to give the thiazolines (**2**).

Scheme 1

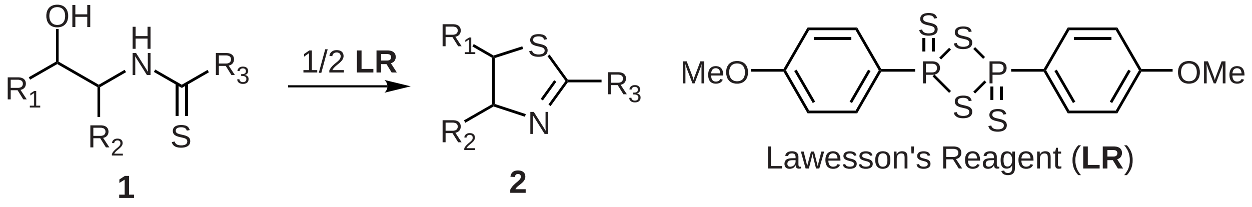


Table 1. Yield of 1,3-Thiazolines (**2**).

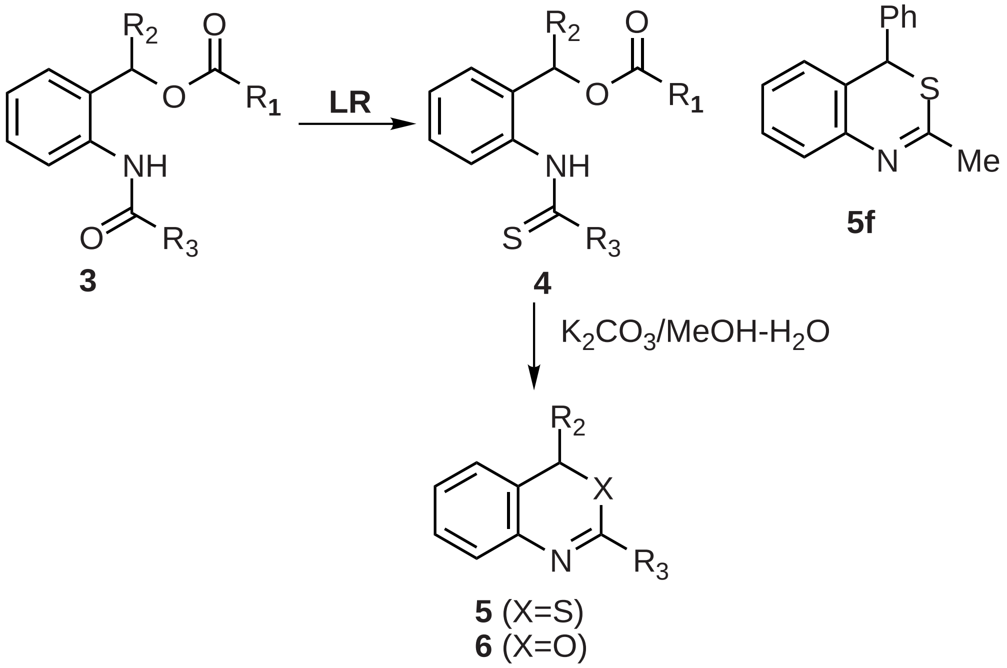
	R^1	R^2	R^3	Yield (%)[a] of **2**
1a	Ph	H	Ph	**2a** (70) [56][b]
1b	Ph	Me	Ph	**2b** (90) [57][b] [72][c]
1c	Ph	H	2-Furyl	**2c** (73) [71][b]
1d	Ph	Me	2-Furyl	**2d** (42) [36][b]
1e	Ph	H	1-Adamantyl	**2e** (91) [52][b]
1f	Ph	Me	1-Adamantyl	**2f** (80) [71][b]
1g	Me	H	Ph	**2g** (28) [11][b]

[a]Isolated yield. [b]Ref. 3i. [c]Ref. 6.

1. *Thionation of N-Acylamino Esters* (**3**) *with* **LR** and *Saponification of N-Thioacylamino Esters* (**4**) *with* K_2CO_3.

N-Acylamino esters (**3a-e, g-h**) were treated with 0.5 equiv. of **LR** under the same conditions as described above to yield the corresponding *N*-thioacylamino esters (**4a-e**, **g-h**), in which acylamino-carbonyl was selectively thionated, in high yields (Scheme 2 and Table 2). This is probably due to the low reactivity of the ester group toward **LR**.[2, 3k-l, n] Similar results were obtained when an equimolar amount of **LR** was used in this reaction. In the case of *N*-acylamino ester (**3f**), 2-methyl-4-phenyl-3,1-benzothiazine (**5f**) was obtained by treatment of **3f** with **LR**. Saponification of *N*-thioacylamino esters (**4**) leading to *N*-thioacylamino alcohols was reported by Lellouche and his coworkers.[6] Therefore, the saponification of *N*-thioacylamino esters (**4**) was investigated with a view to preparing *N*-thioacylamino alcohols. However, when *N*-thioacylamino esters (**4**) were saponified with K_2CO_3 in MeOH-H_2O, 3,1-benzothiazines (**5**) and 3,1-benzoxazines (**6**) were obtained and *N*-thioacylamino alcohols were not isolated (Scheme 2 and Table 3).

Scheme 2



A plausible mechanism for the formation of 3,1-benzothiazines (**5**) and 3,1-benzoxazines (**6**) involves initial saponification of **4** to the corresponding *N*-thioacylamino alcohols followed further changes shown in Scheme 3. Subsequent intramolecular nucleophilic attack of thioamide S-atom to hydroxy group leads to 3,1-benzothiazines (**5**) (path a). On the other hand, *N*-thioacylamino alcohol undergoes ring closure by the nucleophilic attack of OH on the thioamide carbon followed by elimination of H_2S to give 3,1-benzoxazines (**6**) (path b).

Table 2. Yield of Thioamides (**4**) and 3,1-Benzothiazine (**5**) in the Reaction of *N*-Acylamino Esters (**3**) with **LR**.

				Yield (%)[a]	
	R^1	R^2	R^3	**4**	**5**
3a	*p*-Tol	H	*p*-Tol	**4a** (98)	-[b]
3b	*p*-Tol	Ph	*p*-Tol	**4b** (71)	-
3c	Me	H	*p*-Tol	**4c** (85)	-
3d	*t*-Bu	H	*t*-Bu	**4d** (68)	-
3e	Me	H	Me	**4e** (39)	-
3f	Me	Ph	Me	-	**5f** (50)
3g	2-Furyl	H	2-Furyl	**4g** (93)	-
3h	2-Thienyl	H	2-Thienyl	**4h** (87)	-

[a]Isolated yield. [b]Not isolated.

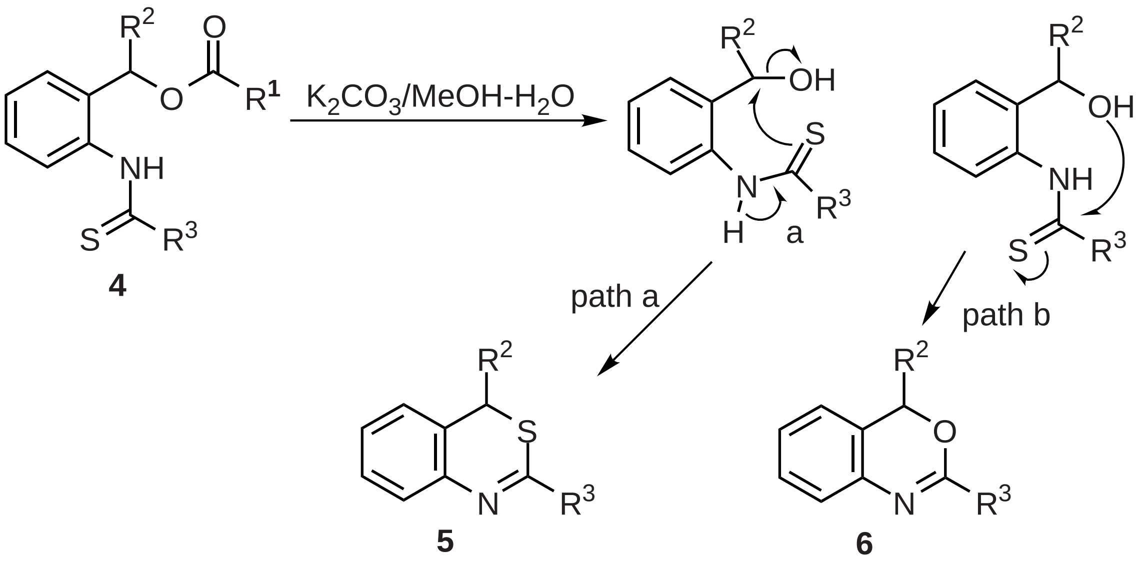
Table 3. Yield of 3,1-Benzothiazines (**5**) and 3,1-Benzoxzines (**6**) by Saponification of *N*-Thioacylamino Esters (**4**) with K_2CO_3.

				Yield (%)[a]	
	R^1	R^2	R^3	**5**	**6**
4a	*p*-Tol	H	*p*-Tol	**5a** (26)	**6a** (37)
4b	*p*-Tol	Ph	*p*-Tol	**5b** (50)	**6b** (24)
4c	Me	H	*p*-Tol	**5c** (tr.)	**6c** (14)
4d	*t*-Bu	H	*t*-Bu	**5d** (24)	-[b]
4g	2-Furyl	H	2-Furyl	**5g** (73)	**6g** (tr.)
4h	2-Thienyl	H	2-Thienyl	**5h** (14)	-
4i	Me	Ph	*p*-Tolyl	**5b** (tr.)	**6b** (94)

[a]Isolated yield. [b]Not isolated

Next we explored the thionation of *o*-(*N*-acylamino)benzyl alcohols (**7**) in the hope of forming *N*-thioacylamino alcohols. Treatment of *o*-(*N*-acylamino)benzyl alcohols (**7**) with **LR** in toluene at the reflux temperature under argon for 15 min gave complex mixtures from which the 3,1-benzothiazines (**5**) and *o*-(*N*-acylamino)phenylmethanethiols (**8**) were isolated and the corresponding *N*-thioacylamino alcohols could not be isolated (Scheme 4 and Table 4). This result is somewhat identical with previously published one by us.[3i]

Scheme 3



Scheme 4

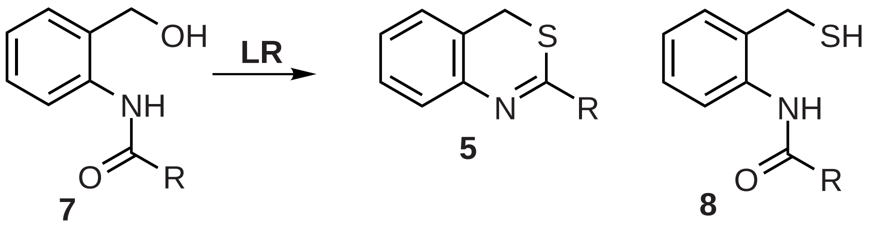


Table 4. Yield of 3,1-Benzothiazines (**5**) and Thiols (**8**) in the Reaction of *o*-(*N*-Acylamino)benzyl alcohols (**7**) with **LR**.

		Molar ratio	Yield (%)[a]	
	R	**LR/7**	**5**	**8**
7a	*p*-Tol	0.5	**5a** (tr.)	**8a** (29)
7a		1	intractable mixture	
7d	*t*-Bu	0.5	**5d** (8)	**8d** (54)
7d		1	**5d** (31)	**8d** (13)
7g	2-Furyl	0.5	-[b]	**8g** (19)
7g		1	-	**8g** (25)

[a] Isolated yield. [b] Not isolated

EXPERIMENTAL

Flash column chromatography was carried out with silica gel Wakogel C-300 or Merck 60. Melting points and boiling points were determined on a Yanaco micro melting-point apparatus (MP-J3) and a Shibata glass tube oven distillation apparatus (GTO-350RD), respectively, and are uncorrected. IR spectra were recorded on a JASCO FT/IR-300 spectrophotometer, in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-EX-270 (270 MHz) or VARIAN GEMINI 200 (200 MHz); measured in CDCl$_3$ using TMS as an internal standard; δ values in ppm, *J* values in Hz.

Reaction of 2-*N*-thioacylamino alcohols (1) with LR: A solution of 2-*N*-thioacylamino alcohols (**1**) (1 mmol) and **LR** (0.5-1 mmol) in toluene (50 mL) was refluxed under argon for 15 min. After removal of the solvent, the residue was chromatographed on a silica gel column with toluene-ethyl acetate (50:1 to 4:1) to give thiazolines (**2**). The structures of the thiazolines (**2**) were confirmed by a direct comparison of their spectral data with those of previously described samples.[3i]

Thionation of *N*-acylamino esters (3) with LR:. A solution of *N*-acylamino esters (**3**) (1 mmol) and **LR** (0.5-1 mmol) in toluene (50 mL) was refluxed under argon for 15 min. After removal of solvent, the residue was chromatographed with toluene-ethyl acetate (50:1 to 4:1) to give the corresponding *N*-thioacylamino esters (**4**) or 3,1-benzothiazine (**5f**). The structure of the **5f** was confirmed by a direct comparison of its spectral data with those of previously described sample.[3i]

o-(*N*-Thiotoluoyl)aminobenzyl toluoate (4a): mp 138-139^{o}C (CHCl$_3$-hexane); IR (KBr) 3221, 1695, 1276, 1117; ^{1}H-NMR δ2.39 (3H, s), 2.40 (3H, s), 5.29 (2H, s), 7.19-7.46 (6H, m), 7.56 (1H, d, *J*=7.6), 7.89-8.01 (5H, m), 10.59 (1H, br s); ^{13}C-NMR δ 21.4, 21.6, 63.4, 126.6, 127.2, 127.4, 129.1, 129.3, 129.8, 131.3, 138.5, 139.0, 142.0, 144.3, 167.3, 199.0. Anal. Calcd for $C_{23}H_{21}NO_2S$: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.81; H, 5.57; N, 3.54.

α-[*o*-(*N*-Thiotoluoyl)aminophenyl]benzyl toluoate (4b): mp 100-101^{o}C (CHCl$_3$-hexane); IR (KBr) 3450, 1616, 1261, 1074; ^{1}H-NMR δ 2.41 (6H, s), 3.86 (1H, s), 7.24-7.47 (13H, m), 8.01 (4H, d, *J*=7.9), 10.41 (1H, br s); ^{13}C-NMR δ 21.4, 21.7, 73.1, 126.3, 126.7, 127.2, 127.8, 127.9, 128.1, 128.5, 129.0, 129.2, 129.3, 138.3, 138.8, 144.5, 166.7, 199.0. Anal. Calcd for $C_{29}H_{25}NO_2S$: C, 77.14; H, 5.58; N, 3.10. Found: C, 77.25; H, 5.58; N, 3.07.

***o*-(*N*-Thiotoluoyl)aminobenzyl acetate (4c):** mp 118-119^{o}C (CHCl$_3$-hexane); IR (KBr) 3235, 1711, 1379, 1242, 1024; ^{1}H-NMR δ 2.05 (3H, s), 2.40 (3H, s), 5.04 (2H, s), 7.23-7.35 (4H, m), 7.41-7.49 (2H, m), 7.94 (2H, d, *J*=7.9), 10.42 (1H, br s); ^{13}C-NMR δ 20.8, 21.4, 63.1, 127.1, 127.3, 127.4, 129.1, 129.3, 129.8, 131.3, 138.3, 138.9, 142.1, 172.0, 198.9. Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.21; H, 5.73; N, 4.68. Found: C, 67.96; H, 5.66; N, 4.50.

***o*-(*N*-Thiopivaloyl)aminobenzyl pivalate (4d):** mp 110-111^{o}C (CHCl$_3$-hexane); IR (KBr) 3263, 1699, 1346, 1165. ^{1}H-NMR δ 1.16 (9H, s), 1.53 (9H, s), 4.95 (2H, s), 7.27-7.46 (3H, m), 7.62-7.66 (1H, m), 9.83 (1H, br s); ^{13}C-NMR δ 27.0, 30.3, 38.6, 45.3, 62.6, 127.5, 128.0, 129.0, 130.7, 138.2, 179.0, 215.0. Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.42; H, 8.20; N, 4.56. Found: C, 66.17; H, 8.02; N, 4.60.

***o*-(*N*-Thioacetyl)aminobenzyl acetate (4e):** bp 170°C(3 mmHg); IR (film) 3210, 1730, 1370, 1235, 1165; ^{1}H-NMR δ 2.08 (3H, s), 2.78 (3H, s), 5.04 (2H, s), 7.27-7.47 (3H, m), 7.82-7.87 (1H, m), 10.15 (1H, br s); ^{13}C-NMR δ 20.8, 35.0, 62.8, 127.1, 127.5, 128.5, 129.3, 131.2, 137.6, 162.3, 201.7. Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.18; H, 5.87; N, 6.23. Found: C, 59.11; H, 5.98; N, 6.47.

***o*-[*N*-(2-Thiofuroyl)amino]benzyl 2-furancarboxylate (4g):** mp 105-106°C ($CHCl_3$-hexane); IR (KBr) 3285, 1700, 1295, 1110; 1H-NMR δ 5.31 (2H, s), 6.50-6.53 (2H, m), 7.24-7.59 (7H, m), 7.93 (1H, d, *J*=7.9), 10.47 (1H, br s); ^{13}C-NMR δ 63.5, 112.0, 113.2, 118.4, 118.8, 127.4, 127.5, 129.2, 129.8, 130.9, 137.0, 143.9, 144.2, 146.8, 152.7, 158.7, 182.2. Anal. Calcd for $C_{17}H_{13}NO_4S$: C, 62.38; H, 4.00; N, 4.28. Found: C, 62.30; H, 3.82; N, 4.02.

***o*-[*N*-(2-Thiothenoyl)amino]benzyl 2-thiophencarboxylate (4h):** mp 153-154°C ($CHCl_3$-hexane); IR (KBr) 3245, 1674, 1343, 1287, 1086; ^{1}H-NMR δ 5.27 (2H, s), 7.08-7.18 (2H, m), 7.24-5.61 (5H, m), 7.84-7.95 (3H, m), 10.78 (1H, br s); ^{13}C-NMR δ 63.6, 124.4, 127.5, 127.7, 128.2, 129.5, 131.7, 132.5, 133.5, 133.8, 134.5, 137.8, 148.0, 163.3, 188.4. Anal. Calcd for $C_{17}H_{13}NO_2S_3$: C, 56.83; H, 3.65; N, 3.90. Found: C, 56.44; H, 3.48; N, 3.69.

Saponification of *N*-thioacylamino esters (4) with K_2CO_3: A solution of *N*-thioacylamino esters (**4**) (1 mmol) and K_2CO_3 (2-4 mmol) in MeOH (10 mL)-H_2O (10 mL) was stirred for 15 h at room temperature. The reaction mixture was poured into water and extracted with methylene chloride. The extract was washed with 10 % HCl solution, water and then dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was chromatographed on a silica gel column with toluene-ethyl acetate (50:1-4:1) to give 3,1-benzothiazines (**5**) and 3,1-benzoxazines (**6**). The structure of 4-phenyl-2-(*p*-tolyl)-3,1-benzothiazime (**5b**) was confirmed by a direct comparison of its spectral data with those of previously described sample.[3i]

2-(*p*-Tolyl)-3,1-benzothiazine (5a): mp 106-107°C ($CHCl_3$-hexane); IR (KBr) 1595, 1534, 1501, 1254, 1171, 1111, 950, 823, 756; ^{1}H-NMR δ 2.41 (3H, s), 3.98 (2H, s), 7.13-7.45 (6H, m), 8.03 (2H, d, *J*=8.3); ^{13}C-NMR δ 21.5, 28.6, 119.7, 126.8, 127.3, 128.2, 128.4, 129.2, 135.3, 142.0, 144.5, 161.0. Anal. Calcd for $C_{15}H_{13}NS$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.39; H, 5.48; N, 5.79.

2-(*p*-Tolyl)-3,1-benzoxazine (6a): mp 102-103°C ($CHCl_3$-hexane); IR (KBr) 1615, 1595, 1250, 1075, 830, 755, 720; ^{1}H-NMR δ 2.39 (3H, s), 5.33 (2H, s), 6.97 (1H, d, *J*=7.3), 7.11-7.32 (5H, m), 8.01 (2H, d, *J*=7.9); ^{13}C-NMR δ 21.5, 66.3, 122.3, 123.6, 124.4, 126.1, 127.9, 128.9, 129.5, 139.8, 141.8, 157.8. Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.55; H, 5.93; N, 6.12.

4-Phenyl-2-(*p*-tolyl)-3,1-benzoxazine (6b): mp 147-148°C ($CHCl_3$-hexane); IR (KBr) 1616, 1953, 1565, 1262, 1074, 829, 762, 699; ^{1}H-NMR δ 2.37 (3H, s), 6.40 (1H, s), 6.82 (1H, d, *J*=7.6), 7.08-7.23 (4H, m), 7.28-7.38 (6H, m), 8.01 (2H, d, *J*=8.3); ^{13}C-NMR δ 22.5, 78.3, 124.8, 125.2, 126.3, 127.3, 128.1, 128.7, 128.9, 129.1, 139.5, 139.8, 141.8, 157.0. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.48; H, 5.73; N, 4.66.

2-(*t*-Butyl)-3,1-benzothiazine (5d): bp 165°C(2 mmHg); IR (film) 1662, 1581, 1568, 1480, 1453, 982, 763, 711; ^{1}H-NMR δ 1.33 (9H, s), 3.82 (2H, s), 7.05-7.09 (1H, m), 7.15-7.22 (1H, m), 7.25-7.29 (2H, m); ^{13}C-NMR δ 28.2, 42.3, 119.7, 126.5, 126.6, 127.1, 128.1, 143.6, 173.7. Anal. Calcd for $C_{12}H_{15}NS$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.47; H, 7.01; N, 6.58.

2-Furyl-3,1-benzothiazine (5g): bp 175°C(2 mmHg); IR (film) 1577, 1536, 1471, 1447, 1205, 971, 885, 761; ^{1}H-NMR δ 3,92 (2H, s), 6.52 (1H, dd, *J*=2.0, 3.6), 7.09-7.16 (2H, m), 7.19-7.26 (1H, m), 7.31-7.38 (1H, m), 7.46 (1H, dd, *J*=1.3, 7.9), 7.62 (1H, dd, *J*=1.0, 2.0); ^{13}C-NMR δ 28.0, 111.9, 115.1, 126.8, 127.4, 128.4, 143.8, 145.6, 149.6, 150.0, 150.9. Anal. Calcd for $C_{12}H_9NOS$: C, 66.97; H, 4.22; N, 6.51. Found: C, 67.14; H, 4.27; N, 6.59.

2-Thienyl-3,1-benzothiazine (5h): bp 210°C(2 mmHg); IR (film) 1660, 1545, 1420, 1200, 915, 820, 765, 710; ^{1}H-NMR δ 3.93 (2H, s), 7.06-7.12 (2H, m), 7.14-7.25 (1H, m), 7.29-7.41 (2H, m), 7.50 (1H, dd, *J*=1.0, 5.0), 7.72 (1H, dd, *J*=1.0, 4.0); ^{13}C-NMR δ28.6, 119.7, 126.6, 126.8, 127.3, 127.6, 128.4, 129.7, 130.6, 143.4, 144.2, 154.1. Anal. Calcd for $C_{12}H_9NS_2$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.17; H, 4.03; N, 6.00.

Thionation of *o*-(*N*-acylamino)benzyl alcohols (7) with LR: .A solution of *o*-(*N*-acylamino)benzyl alcohols (**7**) (1 mmol) and **LR** (0.5-1 mmol) in toluene (50 mL) was refluxed under argon for 15 min. After removal of solvent, the residue was chromatographed with toluene-ethyl acetate (50:1 to 4:1) to give 3,1-benzothiazines (**5**) and/or the corresponding *o*-(*N*-acylamino)phenylmethanethiols (**8**).

***o*-(*N*-Toluoylamino)phenylmethanethiol (8a):** mp 115-116°C ($CHCl_3$-hexane); IR (KBr) 3268, 1645, 1609, 1585, 1520, 1445, 1314, 832, 752; ^{1}H-NMR δ 1.82 (1H, t, *J*=6.6), 2.43 (3H, s), 3.79 (2H, d, *J*=6.6), 7.08-7.16 (1H, m), 7.21-7.37 (4H, m), 7.86-7.90 (2H, m), 8.00-8.33 (1H, m), 8.83 (1H, br s); ^{13}C-NMR δ 21.5, 26.6, 124.3, 125.1, 127.2, 129.1, 129.4, 129.8, 130.9, 131.6, 136.1, 142.5, 165.3. Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.80; H, 5.83; N, 5.26.

***o*-(*N*-Pivaloylamino)phenylmethanethiol (8d):** mp 82-82.5°C ($CHCl_3$-hexane); IR (KBr) 3298, 2559, 1638, 1600, 1509, 1469, 1248, 756, 734; ^{1}H-NMR δ 1.36 (9H, s), 1.75 (1H, t, *J*=6.6), 3.71 (2H, dd, *J*=1.0, 6.6), 7.03-7.18 (1H, m), 7.18 (1H, d, *J*=5.9), 7.25-7.31 (1H, m), 7.86 (1H, d, *J*=8.3), 8.21 (1H, br s); ^{13}C-NMR δ 26.4, 27.6, 39.6, 124.3, 124.9, 128.4, 128.9, 131.0, 136.0, 176.8. Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.55; H, 7.68; N, 6.17. Found: C, 64.68; H, 7.47; N, 6.16.

***o*-(*N*-Furoylamino)phenylmethanethiol (8g):** bp 225°C(2 mmHg); IR (film) 3300, 2558, 1667, 1587, 1518, 1452, 1304, 755; ^{1}H-NMR δ 1.81 (1H, t, *J*=6.6), 3.78 (2H, d, *J*=6.6), 6.54 (1H, dd, *J*=1.7, 3.6), 7.05-7.33 (3H, m), 7.54 (1H, d, *J*=1.7), 7.97 (1H, d, *J*=6.6), 8.87 (1H, br s); ^{13}C-NMR δ 26.1, 112.4, 115.2, 124.1, 125.3, 128.4, 129.1, 131.4, 135.0, 144.4, 147.7, 156.2. Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.47; H, 4.87; N, 5.92

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