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ACYLATION AND ALKOXYCARBONYLATION OF BENZOXAZOLINE-2-THIONE AND BENZOTHIAZOLINE-2-THIONE

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Abstract- Acylation of benzoxazoline-2-thione (**1**) and benzothiazoline-2-thione (**2**) with acetic anhydride (**3**) and acyl chlorides (**4**) gave *N*-acyl (**5, 6**) and/or *S*-acyl (**7, 8**) derivatives depending on the nature of acylating agents and bases used. Alkoxycarbonylation of **1** with aralkyl chlorocarbonates (**9**) gave *N*-alkoxycarbonyl derivatives (**10**) mainly, while that of **2** with aralkyl chloroccarbonates (**9**) gave *S*-alkoxycarbonyl derivatives (**12**) exclusively. Photolysis of *N*-acyl derivatives (**5** or **6**) in the presence of alcohols afforded **1** or **2**, respectively, together with esters (**16**).

INTRODUCTION

A variety of methodologies for activation of carboxy group have been developed. *N*-Acyl and *S*-acyl derivatives of benzoxazoline-2-thione (**1**) and benzothiazoline-2-thione (**2**) have been widely applied as acylating agents for the synthesis of amides, esters and peptides.[1,2] In continuation of our studies on the photochemistry of benzoxazoline-2-thiones[3] and benzothiazoline-2-thiones,[4] we were seeking a simple method for the synthesis on *N*-acyl- (**5**) or *N*-alkoxycarbonylbenzoxazoline-2-thiones (**10**) and *N*-acyl- (**6**) or *N*-alkoxycarbonylbenzothiazoline-2-thiones (**15**). The literature on the synthesis of such compounds by acylation and alkoxycarbonylation of benzoxazoline-2-thione (**1**) and benzothiazoline-2-thione (**2**) is somewhat confusing because of tautomer of **1** and **2** (Scheme 1).[1,2] In this paper we report the reaction of acylation and alkoxycarbonylation of **1** and **2** under various conditions and photochemical behaviour of *N*-acylbenzoxazoline-2-thiones (**5**) and *N*-acylbenzothiazoline-2-thiones (**6**).

RESULTS AND DISCUSSION

1. *Acylation of Benzoxazoline-2-thiones* (**1**) *and Benzothiazoline-2-thione* (**2**).

Benzoxazoline-2-thione (**1**) was heated in acetic anhydride at reflux temperature for 3 h to yield *N*-

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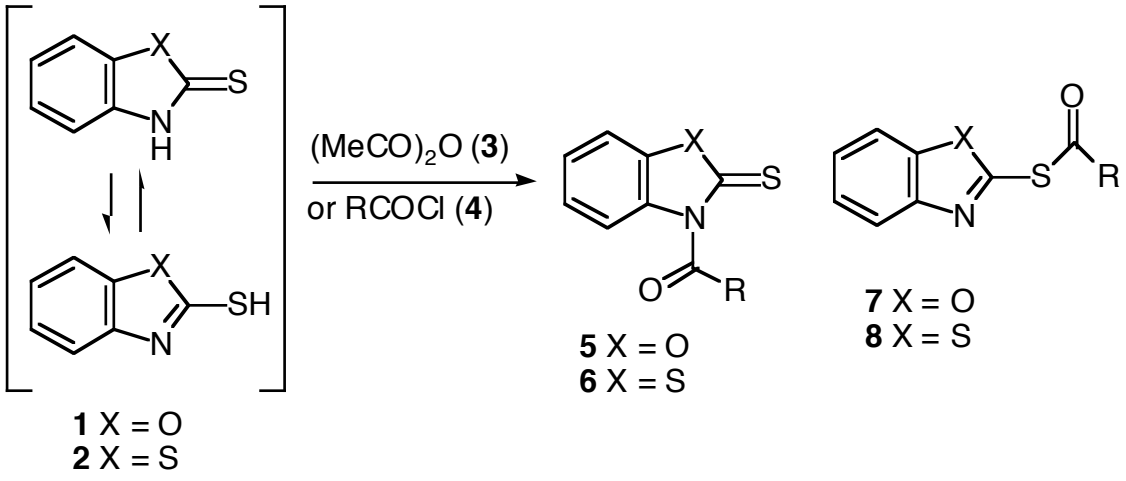
Dedicated to Professor Leo A. Paquette on the occasion of his 70th birthday.

acetylbenzoxazoline-2-thione (**5a**) (*N*-acyl derivative) as the sole product, while benzothiazoline-2-thione (**2**) was heated in acetic anhydride under the same conditions to yield a mixture of two isomers, *N*-acetylbenzothiazoline-2-thione (**6a**) (*N*-acyl derivative) and *S*-(benzothiazol-2-yl) thioacetate (**8a**) (*S*-acyl derivative) (Method A). Treatment of **1** with acyl chloride in the presence of sodium hydride at room temperature gave *N*-acyl derivatives (**5b-c, e-g**), exclusively (Method B). On the contrary, treatment of **1** with benzoyl chloride gave a mixture of both isomers (**5h** and **7h**). *S*-Acyl derivative (**7h**) was obtained as main product when **1** was treated with benzoyl chloride at room temperature. At higher temperature, *N*-acyl derivative (**5h**) was produced predominately. The kinetically controlled product by this reaction is probably *S*-benzoyl derivative (**7h**), which rearranged thermally to yield thermodynamically more stable isomer *N*-benzoyl derivative (**5h**).[2a] Treatment of benzothiazoline-2-thione (**2**) with acetyl chloride yielded *N*- and *S*-acetyl derivatives (**6a**) and (**8a**), while that of **2** with phenylacetyl chloride yielded *N*-phenylacetyl derivative (**6e**) exclusively. Benzothiazoline-2-thione (**2**) was treated with acetyl chloride in the presence of triethylamine to yield *N*- and *S*-acetyl derivatives (**6a**) and (**8a**) (Method C). Benzothiazoline-2-thione (**2**) was treated with acyl chloride to yield *N*-acyl derivatives (**6b, e-h**). However, *S*-pivaloyl derivatives (**7d, 8d**) were obtained by the treatment of thiones (**1**, **2**) with pivaloyl chloride. The structures of **5-8** were assigned on the basis of spectral data and microanalyses. Additional proof for the structures of *N*-acyl derivatives (**5, 6**) of **1** and **2** was obtained through the photochemical behavior as described in section 3.

Scheme 1



2. *Alkoxycarbonylation of Benzoxazoline-2-thione* (**1**) *and Benzothiazoline-2-thione* (**2**).

Alkoxycarbonylation of benzoxazoline-2-thione (**1**) with phenyl and allyl chlorocarbonates (**9**) in the presence of bases such as sodium hydride (Method B) and triethylamine (Method C) gave exclusively *N*-alkoxycarbonyl derivatives (**10c, e**). When **1** was treated with benzyl chlorocarbonate in the presence of triethylamine, both *N*- and *S*-benzyloxycarbonyl derivatives (**10b**) and (**11b**) were obtained in 60 and 30% yields, respectively. Wunsch *et al*. reported *N*-benzyloxycarbonyl derivative (**10b**) was obtained as the

Table 1. Acylation of Benzoxazoline-2-thione (**1**) and Benzothiazoline-2-thione (**2**)

Starting Material		Reagent	Method	Yield (%)[a]	
	X	R		**5**/**6**	**7**/**8**
1	O	Me	A	**5a** (88)	
2	S	Me	A	**6a** (15)	**8a** (26)
2	S		B	**6a** (29)	**8a** (62)
2	S		C	**6a** (33)	**8a** (48)
1	O	*i*-Pr	B	**5b** (98)	
2	S	*i*-Pr	C	**6b** (93)	
1	O	*i*-Bu	B	**5c** (81)	
1	O	*t*-Bu	C		**7d** (95)
2	S	*t*-Bu	C		**8d** (95)
1	O	$PhCH_2$	B	**5e** (61)	
2	S	$PhCH_2$	B	**6e** (95)	
2	S		C	**6e** (21)	
1	O	$PhCH_2CH_2$	B	**5f** (92)	
2	S	$PhCH_2CH_2$	C	**6f** (85)	
1	O	$PhOCH_2$	B	**5g** (35)	
2	S	$PhOCH_2$	C	**6g** (83)	
1	O	Ph	B	**5h** (12)	**7h** (87)
1	O		B[b]	**5h** (92)	**7h** (8)
2	S	Ph	C	**6h** (89)	

[a]Isolated yield. [b]Reflux, 3 h.

Method A: $(CH_3CO)_2O$, Reflux, 2 h.

Method B: RCOCl/NaH, rt, 2-5 h.

Method C: RCOCl/Et_3N, rt, 1 h.

sole product in the reaction of **1** with benzyl chlorocarbonate under similar conditions.[2b] On the other hand, alkoxycarbonylation of benzothiazoline-2-thione (**2**) with alkyl, phenyl, and allylchlorocarbonates (**9**) in the presence of bases such as sodium hydride, triethylamine, and sodium carbonate (Method D) gave exclusively *S*-alkoxycarbonyl derivatives (**12a-e**). The structures of *N*- and *S*-alkoxycarbonyl derivatives (**10-12**) were determined on the basis of spectral data and elemental analyses. The result obtained for **12b** differed from literature data published earlier by Wunsch *et al*.[5] The IR and NMR

spectra of *N*-methoxycarbonyl- and *N*-benzyloxycarbonylbenzothiazoline-2-thiones (**15a, b**) prepared by thiation of *N*-alkoxycarbonylbenzothiazolin-2-ones (**14a, b**) with Lawesson's reagent (Scheme 3) ensured the assignment of the *S*-alkoxycarbonyl derivatives(**12a**, **b**).

Scheme 2

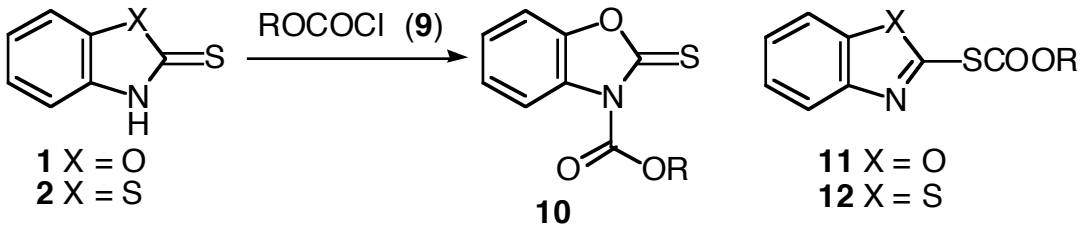


Table 2. Alkoxycarbonylation of Benzoxazoline-2-thione (**1**) and Benzothiazoline-2-thione(**2**)

Starting Material		Reagent	Method	Yield (%)[a]	
	X	R		**10**	**11/12**
2	S	Me	C		**12a** (89)
1	O	$PhCH_2$	C	**10b** (60)	**11b** (30)
2	S	$PhCH_2$	B		**12b** (quant)
2	S	$PhCH_2$	C		**12b** (quant)
1	O	Ph	C	**10c** (92)	
2	S	Ph	C		**12c** (quant)
2	S	9-Fluorenylmethyl	D		**12d** (77)
1	O	Allyl	B	**10e** (95)	
2	S	Allyl	C		**12e** (quant)

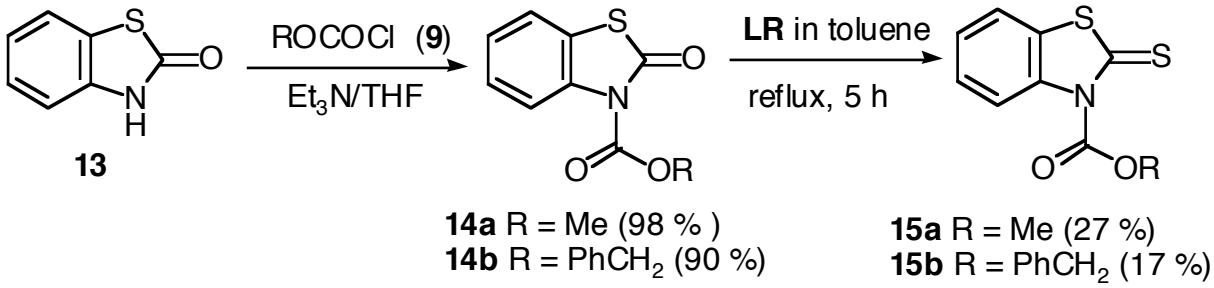
[a]Isolated yield.

Method B: ROCOCl/NaH, rt, 1 h.

Method C: ROCOCl/Et_3N, rt, 1 h.

Method D: ROCOCl/Na_2CO_3, rt, 1 h.

Scheme 3



3. *Photolysis of N-Acylbenzoxazoline-2-thiones* (**5**) *and N-Acylbenzothiazoline-2-thiones* (**6**)**.**

N-Acylbenzoxazoline-2-thiones (**5**) and *N*-acylbenzothiazoline-2-thiones (**6**) are stable at room temperature. However, upon irradiation with a high-pressure mercury lamp, these compounds undergo cleavage of the acyl substituent to give benzoxazoline-2-thione (**1**) and benzothiazoline-2-thione (**2**), respectively. Irradiation of **5a** or **6a** in $CDCl_3$ in the presence of a few drops of EtOH gave ethyl acetate (**16a**) and **1** or **2**, respectively (Table 3). Similarly, the corresponding ethyl esters (**16b**, **c, e-g**) were obtained along with the thione (**1** or **2**) when **5b-c, e-g** or **6b, e-f** were irradiated under the same conditions. Irradiation of **6e** in benzene in the presence of alcohols such as MeOH, EtOH and *iso*-PrOH in preparative scale gave the corresponding esters (**16e, h-i**) and benzothiazoline-2-thione (**2**) in excellent yields (Scheme 5). The formation of esters (**16a-c, e-i**) is shown in Scheme 6, involving intermediates (**B**) and (**C**). A ketene intermediate (**C**) reacted alcohols to yield the corresponding esters (**16**). Analogous □-hydrogen abstractions were observed in the photolysis of *N*-acyl-2-thionothiazolidines[6] and *N*-acylindoline-2-thiones.[7]

Scheme 4

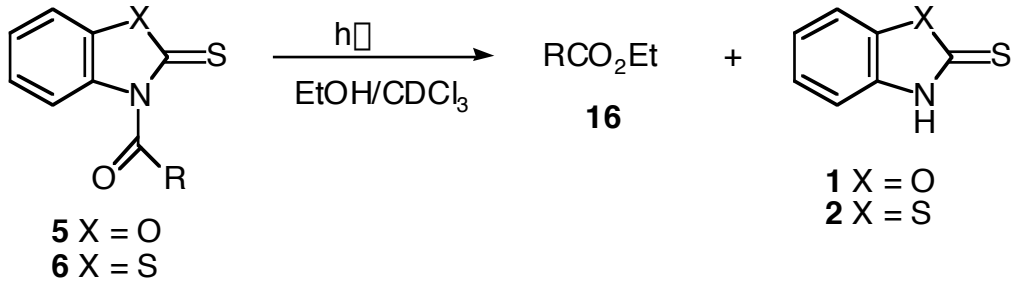
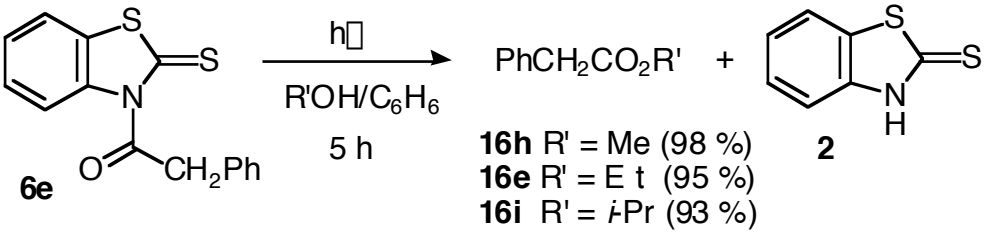


Table 3. Photolysis of *N*-Acylbenzoxzoline-2-thiones (**5**) and *N*-acylbenzothiazoline-2-thiones (**6**).

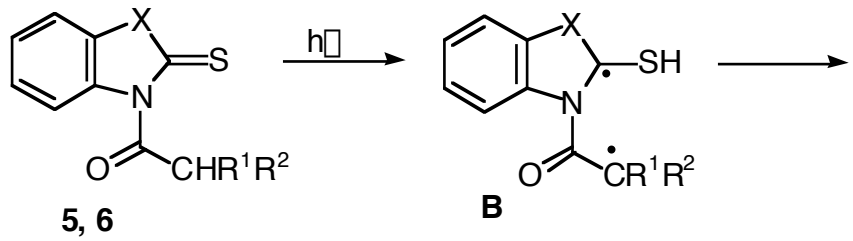
Thione		Irr. time	Yield (%)[a]		
	R	(h)	**16**	**1**/**2**	Rec.
5a	Me	15	**16a** (46)	**1** (46)	**5a** (54)
6a	Me	5	**16a** (>95)	**2** (>95)	**6a** (~0)
5b	*i*-Pr	20	**16b** (71)	**1** (71)	**5b** (29)
6b	*i*-Pr	6.5	**16b** (>95)	**2** (95)	**6b** (~0)
5c	*i*-Bu	20	**16c** (27)	**1** (27)	**5c** (73)
5e	$PhCH_2$	5	**16e** (>95)	**1** (>95)	**5e** (<5)
6e	$PhCH_2$	5	**16e** (>95)	**2** (>95)	**6e** (~0)
5f	$PhCH_2CH_2$	20	**16f** (64)	**1** (64)	**5f** (34)
6f	$PhCH_2CH_2$	5	**16f** (>95)	**2** (>95)	**6f** (~0)
5g	$PhOCH_2$	20	**16g** (64)	**1** (64)	**5g** (36)
6g	$PhOCH_2$	3	**16g** (>95)	**2** (>95)	**6g** (~0)

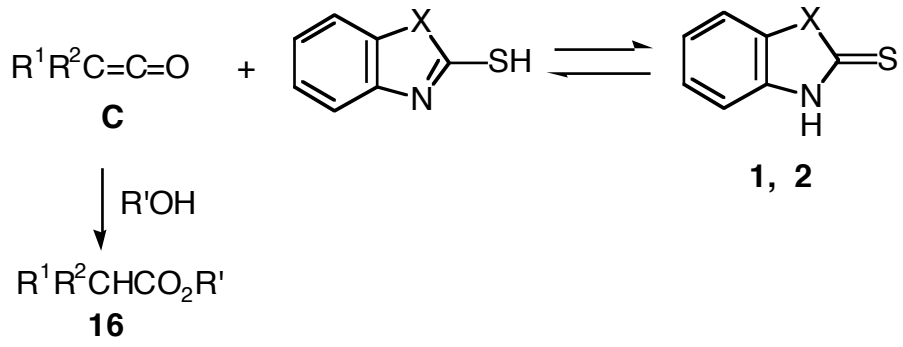
[a]Yield was determined by ^{1}H-NMR spectrometry.

Scheme 5



Scheme 6





EXPERIMENTAL

Flash chromatography was carried out with silica gel (Wakogel C-300 or Merck 60). Melting 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 uncorrected. IR spectra were recorded with JASCO FT/IR-300 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded with JEOL JNM-EX-270 (270 MHz) and Varian GEMINI 200 (200 MHz) with $CDCl_3$ as solvent and Me_4Si as an internal standard; *J*-values are expressed in Hz.

Acylation of Benzoxazoline-2-thione (1) and Benzothiazoline-2-thione (2). General Procedure. **Method A:** A solution of **1** (or **2**) (10 mmol) in acetic anhydride (20 mL) was refluxed under argon for 2 h and then poured into water. Product was extracted with ethyl acetate, and the solution was worked up. After removal of the solvent, the residue was recrystallized from $CHCl_3$-hexane or chromatographed on a silica gel column with toluene/ethyl acetate 4:1 to yield *N*-acyl (**5, 6**) and *S*-acyl derivatives (**8**). **Method B:** To a solution of **1** (or **2**) (10 mmol) and NaH (15 mmol-equiv.) in THF (30 mL)/benzene (20 mL) was added a solution of acyl chloride (**4**) (12 mmol) in benzene (20 mL) dropwise with stirring in an ice bath and the mixture was stirred for 2-5 h at rt under argon. Usual work-up gave *N*-acyl (**5, 6**) and/or *S*-acyl derivatives (**7, 8**). **Method C:** To a solution of **1** (or **2**) (10 mmol) and Et_3N (25 mmol) in CH_2Cl_2 (30 mL)/benzene (20 mL) was added a solution of **4** (15 mmol) in benzene (20 mL) dropwise in an ice bath under argon. The mixture was stirred at rt for 1 h and then usual work-up gave **6-8**.

***N*-Acetylbenzoxazoline-2-thione (5a):** mp 119-120°C ($CHCl_3$/*n*-hexane) (lit.,[2a] mp 120-121°C); IR (KBr) 1740 (C=O); ^{1}H-NMR δ 3.05 (*s*, 3H), 7.26-7.35 (*m*, 3H), 8.05-8.10 (*m*, 1H); ^{13}C-NMR δ 27.8, 109.6, 116.5, 125.5, 126.2, 129.8, 146.4, 170.9, 179.2.

***N*-Acetylbenzothiazoline-2-thione (6a):** mp 73-74°C ($CHCl_3$/*n*-hexane); IR (KBr) 1740 (C=O); ^{1}H-NMR δ 2.56 (*s*, 3H), 7.26-7.62 (*m*, 2H), 7.88-7.92 (*m*, 1H), 8.02-8.06 (*m*, 1H). ^{13}C-NMR δ 30.6, 121.2, 123.1, 125.6, 126.3, 127.2, 136.1, 151.6, 190.6. Anal. Calcd for $C_9H_7NOS_2$: C, 51.64; H, 3.37; N, 6.69. Found: C, 51.99; H, 3.25; N, 7.01.

***S*-(Benzothiazol-2-yl) Thioacetate (8a):** mp 75-75.5°C ($CHCl_3$/*n*-hexane); IR (KBr) 1720 [C(=O)-S]; ^{1}H-

NMR δ 2.98 (*s*, 3H), 7.30-7.43 (*m*, 3H), 7.57-7.62 (*m*, 1H); ^{13}C-NMR δ 28.1, 115.0, 120.8, 125.8, 127.3, 128.1, 139.7, 157.4, 173.2. Anal. Calcd for $C_9H_7NOS_2$: C, 51.64; H, 3.37; N, 6.69. Found: C, 51.48; H, 3.26; N, 6.85.

***N*-(*iso*-Butyryl)benzoxazoline-2-thione (5b):** mp 194-195°C ($CHCl_3$/*n*-hexane); IR (KBr) 1715 (C=O); ^{1}H-NMR δ 1.34 (*d*, *J* = 6.6, 3H), 1.35 (*d*, *J* = 6.6, 3H), 4.78-4.82 (*m*, 1H), 7.27-7.36 (*m*, 3H), 7.94-8.00 (*m*, 1H); ^{13}C-NMR δ 18.8, 34.6, 109.6, 116.0, 125.5, 125.9, 130.3, 146.5, 178.4, 178.5. Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 59.70; H, 5.01; N, 6.33. Found: C, 59.67; H, 4.99; N, 6.30.

***N*-(*iso*-Butyryl)benzothiazoline-2-thione (6b):** mp 170-171°C ($CHCl_3$/*n*-hexane). IR (KBr) 1700 (C=O); ^{1}H-NMR δ 1.33 (*d*, *J* = 6.9, 6H), 2.95 (*sept*. *J* = 6.9, 1H), 7.37-7.52 (*m*, 2H), 7.87-7.91 (*m*, 1H), 8.01-8.05 (*m*, 1H); ^{13}C-NMR δ 19.0, 43.6, 121.1, 122.9, 125.4, 126.2, 136.1, 151.6, 157.7, 198.6. Anal. Calcd for $C_{11}H_{11}NOS_2$: C, 55.66; H 4.67; N, 5.90. Found: C 55.53; H, 4.33; N, 5.60.

***N*-(*iso*-Valeryl)benzoxazoline-2-thione (5c):** mp 72-72°C ($CHCl_3$/*n*-hexane); IR (KBr) 1735 (C=O); ^{1}H-NMR δ 1.07 (*d*, *J* = 6.6, 3H), 1.08 (*d*, *J* = 6.6, 3H), 2.31-2.42 (*m*, 1H), 3.41 (*d*, *J* = 6.9, 2H), 7.26-7.37 (*m*, 3H), 8.05-8.09 (*m*, 1H); ^{13}C-NMR δ 22.4, 25.1, 43.7, 109.6, 116.3, 125.5, 126.0, 130.0, 146.5, 173.4, 178.8. Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95. Found: C, 61.17; H, 5.52; N, 5.92.

***S*-(Benzoxazol-2-yl) Thiopivalate (7d):** mp 169-170°C ($CHCl_3$/*n*-hexane); IR (KBr) 1735 [C(=O)-S]; ^{1}H-NMR δ 1.36 (*s*, 9H), 7.35-7.41 (*m*, 2H), 7.55-7.59 (*m*, 1H), 7.77-7.81 (*m*, 1H); ^{13}C-NMR δ 27.0, 48.1, 110.8, 120.4, 124.7, 126.0, 141.9, 152.8, 156.0, 200.0. Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95. Found: C, 61.55; H, 5.72; N, 5.74.

***S*-(Benzothiazol-2-yl) Thiopivalate (8d):** mp 56-57°C ($CHCl_3$/*n*-hexane); IR (KBr) 1690 [C(=O)-S]; ^{1}H-NMR δ 1.38 (*s*, 9H), 7.38-7.52 (*m*, 2H), 7.88-7.92 (*m*, 1H), 8.02-8.06 (*m*, 1H); ^{13}C-NMR δ 27.1, 47.2, 121.2, 123.0, 125.4, 126.2, 137.3, 152.8, 157.5, 168.1. Anal. Calcd for $C_{12}H_{13}NOS_2$: C, 57.33; H, 5.21; N, 5.57. Found: C, 57.35; H, 5.22; N, 5.58.

***N*-(Phenylacetyl)benzoxazoline-2-thione (5e):** mp 117-119°C ($CHCl_3$/*n*-hexane); IR (KBr) 1730 (C=O); ^{1}H-NMR δ 4.89 (*s*, 2H), 7.21-7.41 (*m*, 8H), 8.02-8.05 (*m*, 1H); ^{13}C-NMR δ 45.3, 109.7, 116.4, 125.6, 126.2, 127.5, 128.7, 129.8, 132.5, 146.5, 172.3, 178.7; Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N 5.20. Found: C, 67.06; H, 4.12; N 5.36.

***N*-(Phenylacetyl)benzothiazoline-2-thione (6e):** mp 168-170°C ($CHCl_3$/*n*-hexane); IR (KBr) 1710 (C=O); ^{1}H-NMR δ 4.01 (*s*, 2H), 7.21-7.51 (*m*, 7H), 7.85-7.89 (*m*, 1H), 7.99-8.03 (*m*, 1H); ^{13}C-NMR δ 50.4, 121.2, 123.0, 125.6, 126.3, 128.1, 128.9, 129.9, 131.7, 135.9, 151.6, 157.6, 192.6. Anal. Calcd for $C_{15}H_{11}NOS_2$ (285.32): C, 63.14; H, 3.89; N, 4.91. Found: C, 63.48; H, 4.03; N, 4.99.

***N*-(Phenylpropionyl)benzoxazoline-2-thione (5f):** mp 87-88°C ($CHCl_3$/*n*-hexane); IR (KBr) 1725 (C=O); ^{1}H-NMR δ 3.10 (*t*, *J* = 7.3, 2H), 3.78 (*t*, *J* = 7.3, 2H), 7.17-7.31 (*m*, 8H), 7.99-8.01 (*m*, 1H). ^{13}C-NMR δ 30.1, 40.6, 109.5, 116.3, 125.4, 125.9, 126.3, 128.4, 128.5, 129.7, 139.8, 146.3, 170.0, 178.4. Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 67.82; H, 4.62; N 4.94. Found: C, 67.55; H, 4.64; N 4.95.

***N*-(Phenylpropionyl)benzothiazoline-2-thione (6f):** mp 71-72°C ($CHCl_3$/*n*-hexane); IR (KBr) 1715 (C=O); ^{1}H-NMR δ 3.08 (*br s*, 4H), 7.18-7.52 (*m*, 7H), 7.86-7.90 (*m*, 11H), 8.00-8.04 (*m*, 1H); ^{13}C-NMR δ 30.8, 45.5, 121.1, 122.9, 125.5, 126.3, 126.5, 128.3, 128.6, 136.0, 139.0, 151.4, 157.2, 193.3. Anal. Calcd For $C_{16}H_{13}NOS_2$: C, 64.18; H, 4.38; N, 4.68. Found: C, 63.98; H, 4.34; N, 4.58.

***N*-(Phenoxyacetyl)benzoxazoline-2-thione (5g):** mp 121-122°C ($CHCl_3$/*n*-hexane); IR (KBr) 1740 (C=O); ^{1}H-NMR δ 5.71 (*s*, 2H), 6.99-7.05 (*m*, 3H), 7.24-7.40 (*m*, 5H), 8.13-8.18 (*m*, 1H); ^{13}C-NMR δ 69.5, 109.8, 114.8, 116.5, 122.0, 125.9, 126.6, 129.5, 129.7, 147.1, 157.5, 169.2, 178.0. Anal. Calcd for $C_{15}H_{11}NO_3S$: C, 63.14; H, 3.89; N, 4.91. Found: C, 63.05; H, 3.95; N 4.76.

***N*-(Phenoxyacetyl)benzothiazoline-2-thione (6g):** mp. 68-69°C ($CHCl_3$/*n*-hexane); IR (KBr) 1690 (C=O); ^{1}H-NMR δ 4.86 (*s*, 2H), 6.96-7.10 (*m*, 3H), 7.26-7.53 (*m*, 4H), 7.87-7.92 (*m*, 1H), 8.02-8.06 (*m*, 1H); ^{13}C-NMR δ 70.6, 115.0, 121.2, 122.7, 123.1, 125.7, 126.4, 129.6, 136.3, 151.8, 155.8, 157.2, 194.5. Anal. Calcd for $C_{15}H_{11}NO_2S_2$: C, 59.77; H, 3.68; N 4.65. Found: 59.94; H, 3.68; N, 4.51.

***N*-Benzoylbenzoxzoline-2-thione (5h):** mp 117-118°C ($CHCl_3$/*n*-hexane) (lit.,[2a] mp 117-118°C); IR (KBr) 1695 (C=O); ^{1}H-NMR δ 7.26-7.59 (*m*, 6H), 7.65-7.72 (*m*, 1H), 7.88-7.93 (*m*, 2H); ^{13}C-NMR δ 110.3, 112.8, 125.3, 125.6, 128.8, 130.5, 131.4, 134.6, 147.3, 168.1, 179.1.

***S*-(Benzoxazol-2-yl) Thiobenzoate (7h):** mp 83-84°C ($CHCl_3$/*n*-hexane) (lit.,[2a] mp 83-85°C); IR (KBr) 1695 [C(=O)-S]; ^{1}H-NMR δ 7.35-7.70 (*m*, 6H), 7.79-7.87 (*m*, 1H), 7.95-8.00 (*m*, 2H); ^{13}C-NMR δ 110.9, 120.5, 124.8, 126.2, 127.9, 129.1, 134.8, 135.1, 141.8, 152.8, 154.9, 185.3.

***N*-Benzoylbenzothiazoline-2-thione (6h):** mp 101-102°C ($CHCl_3$/*n*-hexane); IR (KBr) 1670 (C=O); ^{1}H-NMR δ 7.40 (*m*, 5H), 7.92-8.09 (*m*, 4H); ^{13}C-NMR δ 121.1, 123.0, 125.6, 126.3, 127.7, 129.1, 134.6, 135.5, 136.1, 151.7, 186.9. Anal. Calcd for $C_{14}H_9NOS_2$: C, 61.96; H, 3.34; N, 5.16. Found: C, 61.97; H, 3.27; N, 5.08.

Alkoxycarbonylation of Benzoxazoline-2-thiones (1) and Benzothiazoline-2-thiones (2). General Procedure. **Method B:** To a solution of **1** (or **2**) (10 mmol) and NaH (15 mmol-equiv.) in THF (30 mL)/benzene (20 mL) was added a solution of alkoxycarbonyl chloride (**9**) (11 mmol) in benzene (15 mL) dropwise in an ice bath under argon and then the mixture was stirred at rt for 1 h. Usual work-up gave *N*-(**10**) and *S*-alkoxycarbonyl products (**12**). **Method C:** To a solution of **1** (or **2**) (10 mmol) and Et_3N (25 mmol) in benzene (20 mL) was added a solution of **9** (12 mmol) in benzene (20 mL) dropwise in an ice bath under argon and then the mixture was stirred at rt for 1 h. Usual work-up yielded **10-12**. **Method D:** To a solution of **2** (10 mmol) and sodium carbonate (6 mmol) in ethyl acetate (30 mL) was added a solution of **9** (12 mmol) in benzene (20 mL) dropwise in an ice bath under argon and then the mixture stirred at rt for 1 h. Usual work-up yielded **12**.

***S*-(Benzothiazol-2-yl) Methyl Thiocarbonate (12a):** mp 45-45.5°C ($CHCl_3$/*n*-hexane); IR (KBr) 1725 [S-C(=O)-O]; ^{1}H-NMR δ 3.96 (*s*, 3H), 7.38-7.52 (*m*, 2H), 7.88 (*d*, *J* = 7.6), 8.02 (*d*, *J* = 7.6); ^{13}C-NMR δ 55.4, 121.1, 123.0, 123.6, 126.4, 136.4, 152.0, 157.7, 166.7; MS m/z = 225 [M^+], 186, 166, 148, 108.

Anal. Calcd for $C_9H_7NO_2S_2$: C, 47.98; H, 3.13; N, 6.22. Found: C, 48.24; H, 3.16; N, 6.24.

***N*-(Benzyloxycarbonyl)benzoxazoline-2-thione (10b):** mp 87-88°C ($CHCl_3$/*n*-hexane) (lit.,[2b] mp 89-92°C); IR (KBr) 1750 [C(=O)-O]; ^{1}H-NMR δ 5.54 (*s*, 2H), 7.21-7.46 (*m*, 6H), 7.52-7.58 (*m*, 2H), 7.65-7.73 (*m*, 1H); ^{13}C-NMR δ 70.4, 110.0, 115.1, 125.3, 125.9, 128.7, 129.0, 129.1, 133.7, 146.2, 149.7, 176.7.

***S*-(Benzoxazol-2-yl) Benzyl Thiocarbonate (11b):** mp 86-87°C ($CHCl_3$/*n*-hexane); IR (KBr) 1735 [S-C(=O)-O]; ^{1}H-NMR δ 5.31 (*s*, 2H), 7.32-7.45 (*m*, 7H), 7.55-7.59 (*m*, 1H), 7.76-7.80 (*m*, 1H); ^{13}C-NMR δ 71.0, 110.9, 120.6, 124.9, 126.4, 128.6, 129.0, 133.9, 141.5, 152.5, 154.5, 164.3. Anal. Calcd for $C_{15}H_{11}NO_3S$: C, 63.14; H, 3.89; N, 4.91. Found: C, 63.05; H, 3.98; N, 4.90.

***S*-(Benzothiazol-2-yl) Benzyl Thiocarbonate (12b):** mp 88-89°C ($CHCl_3$/*n*-hexane) (lit.,[2b] mp 87°C); IR (KBr) 1730 [S-C(=O)-O]; ^{1}H-NMR δ 5.36 (*s*, 2H), 7.35-7.52 (*m*, 7H), 7.85-7.90 (*m*, 1H), 8.01 (*d*, *J* = 6.3, 1H); ^{13}C-NMR δ 70.6, 121.1, 123.0, 125.6, 126.4, 129.0, 134.0, 136.4, 152.0, 157.7, 166.2; MS m/z = 301 [M^+], 257, 224, 166, 91.

***N*-(Phenoxycarbonyl)benzoxazoline-2-thione (10c):** mp 149-150°C ($CHCl_3$/*n*-hexane); IR (KBr) 1780 [C(=O)-S]; ^{1}H-NMR δ 7.18-7.52 (*m*, 8H), 7.81-7.87 (*m*, 1H); ^{13}C-NMR δ 110.1, 115.2, 120.8, 121.1, 125.4, 126.2, 127.0, 129.8, 146.3, 148.3, 149.7, 176.4. Anal. Calcd for $C_{14}H_9NO_3S$: C, 61.98; H, 3.34; N, 5.16. Found: C, 61.97; H, 3.27; N, 5.08.

***S*-(Benzothiazol-2-yl) Phenyl Thiocarbonate (12c):** mp 83-85°C ($CHCl_3$/*n*-hexane); IR (KBr) 1735 [S-C(=O)-O]; ^{1}H-NMR δ 7.20-7.53 (*m*, 7H), 7.89-7.90 (*m*, 1H), 8.02-8.06 (*m*, 1H); ^{13}C-NMR δ 121.0, 121.2, 123.1, 125.7, 126.5, 126.8, 129.7, 136.5, 150.8, 152.0, 157.1, 165.4. Anal. Calcd for $C_{14}H_9NO_2S_2$: C, 58.53; H, 3.16; N, 4.88. Found: C, 58.84; H, 3.26; N, 4.86.

***S*-(Benzothiazol-2-yl) 9-Fluorenylmethyl Thiocarbonate (12d):** mp 100.5-101°C ($CHCl_3$/*n*-hexane) (lit.,[2b] m.p. 96-98°C); IR (KBr) 1705 [S-C(=O)-O]; ^{1}H-NMR δ 4.30 (*t*, *J* = 7.3, 1H), 4.61 (*d*, *J* = 7.3, 2H), 7.23-7.59 (*m*, 8H), 7.71-7.74 (*m*, 2H), 7.84-7.88 (*m*, 1H), 8.01-8.05 (*m*, 1H); ^{13}C-NMR δ 46.5, 70.6, 120.1, 123.2, 125.0, 125.7, 126.4, 127.2, 128.0, 136.7, 141.2, 142.7, 152.1, 157.2, 166.2.

***N*-(Allyloxycarbonyl)benzoxazoline-2-thione (10e):** mp 64-65°C ($CHCl_3$/*n*-hexane); IR (KBr) 1740 [C(=O)-S], 1650 (C=C); ^{1}H-NMR δ 5.02 (*dd*, *J* = 1.0, 5.9, 2H), 5.43 (*dd*, *J* = 1.0, 10.8, 1H), 5.59 (*dd*, *J* = 1.0, 17.2, 1H), 6.02-6.17 (*m*, 1H), 7.28-7.34 (*m*, 3H), 7.73-7.78 (*m*, 1H); ^{13}C-NMR δ 69.2, 110.0, 115.1, 120.8, 125.3, 126.0, 129.1, 130.1, 146.3, 149.6, 176.7. Anal. Calcd for $C_{11}H_9NO_3S$: C, 56.15; H, 3.86; N 5.96. Found: C, 56.26; H, 3.64; N, 5.86.

***S*-(Benzothiazol-2-yl) Allyl Thiocarbonate (12e):** mp <30°C; IR (KBr) 1725 [S-C(=O)-O], 1650 (C=C); ^{1}H-NMR δ 4.82-4.86 (*m*, 2H), 5.31-5.46 (*m*, 2H), 5.88-6.08 (*m*, 1H), 7.37-7.52 (*m*, 2H), 7.86-7.90 (*m*, 1H), 8.00-8.04 (*m*, 1H); ^{13}C-NMR δ 69.4, 120.4, 121.1, 123.0, 125.5, 126.3, 130.4, 136.4, 152.0, 157.7, 165.9. Anal. Calcd for $C_{11}H_9NO_2S_2$: C, 52.56; H, 3.61; N, 5.58. Found: C, 52.81; H, 3.83; N, 5.58.

Alkoxycarbonylation of Benzothiazolin-2-one (13): To a solution of **13** (10 mmol) and Et_3N (25 mmol)

in THF (15 mL) was added a solution of **9** (15 mmol) in THF (15 mL) dropwise in an ice bath under argon, then the whole was stirred for 2 h at rt, and usual work-up gave *N*-alkoxycarbonylbenzothiazolin-2-ones (**14**).

***N*-(Methoxycarbonyl)benzothiazolin-2-one (14a)**: bp 195°C/2 Torr; mp. 32°C; IR (KBr) 1745, 1720 (C=O); ^{1}H-NMR δ 4.08 (*s*, 3H), 7.21-7.39 (*m*, 3H), 7.99 (*d*, *J* = 8.2, 1H); ^{13}C-NMR δ 54.8, 116.4, 121.6, 122.1, 125.2, 126.9, 134.0, 150.9, 167.9. Anal. Calcd for $C_9H_7NO_3S$: C, 52.66; H, 3.37; N, 6.70. Found: C, 52.51; H, 3.28; N 6.60.

***N*-(Benzyloxycarbonyl)benzothiazolin-2-one (14b):** mp 55-56°C ($CHCl_3$/*n*-hexane); IR (KBr) 1740, 1710 (C=O); ^{1}H-NMR δ 5.48 (*s*, 2H), 7.18-7.44 (*m*, 7H), 7.49-7.53 (*m*, 1H), 7.93-7.98 (*m*, 1H); ^{13}C-NMR δ 67.9, 116.3, 121.5, 122.1, 126.8, 128.3, 128.7, 134.0, 134.3, 150.1, 173.6. Anal. Calcd for $C_{15}H_{11}NO_3S$: C, 63.14; H, 3.89; N 4.91. Found: C, 62.93; H, 3.87; N, 4.78.

Thiation of *N*-(Alkoxycarbonyl)benzothiazolin-2-one (14) with Lawesson's Reagent (LR): A solution of **14** (5 mmol) and **LR** (5.5 mmol) in toluene (50 mL) was refluxed for 5 h under argon. After removal of the solvent, the residue was chromatographed on a silica gel column with toluene/ethyl acetate (50:1) to yield the corresponding thiones (**15**).

***N*-(Methoxycarbonyl)benzothiazoline-2-thione (15a):** mp 46-48°C ($CHCl_3$/*n*-hexane); IR (KBr) 1750 (C=O); ^{1}H-NMR δ 4.15 (*s*, 3H), 7.26-7.49 (*m*, 4H); ^{13}C-NMR δ 55.7, 114.1, 120.9, 125.7, 127.3, 127.4, 134.0, 139.2, 150.7, 189.5; MS m/z = 225 [M^+], 181, 166, 148, 108. Anal. Calcd for $C_9H_7NO_2S_2$: C, 47.98; H, 3.13; N, 6.22. Found: C, 48.22; H, 3.15; N 6.13.

***N*-(Benzyloxycarbonyl)benzothiazoline-2-thione (15b)**: mp 72-72.5°C ($CHCl_3$/*n*-hexane); IR (KBr) 1765 (C=O); ^{1}H-NMR δ 5.54 (*s*, 2H), 7.23-7.45 (*m*, 7H), 7.49-7.55 (*m*, 2H); ^{13}C-NMR δ 71.3, 114.0, 120.8, 125.6, 127.2, 127.4, 128.7, 128.9, 129.1, 133.4, 139.3, 150.2, 189.3; MS m/z = 301 [M^+]; Anal. Calcd for $C_{15}H_{11}NO_2S_2$: C, 59.77; H, 3.68; N, 4.65. Found: C, 59.56; H, 3.74; N, 4.40.

Photolysis of *N*-Acylbenzoxazoline-2-thiones (5) and *N*-Acylbenzothiazoline-2-thiones (6): **Analytical Irradiation**: A solution of **5** (or **6**) (50 mg) in $CDCl_3$ (0.4 mL) containing a few drops of EtOH in a NMR-tube was irradiated under argon with a high-pressure mercury lamp (500 W) at rt for 3-20 h. Photoproducts (**1, 2**, **16**) were proven to be identical with their authentic samples by direct comparison of their ^{1}H- and ^{13}C-NMR spectra. Yields were determined by ^{1}H-NMR analysis. **Preparative Irradiation:** A solution of *N*-(phenylacetyl)benzothiazoline-2-thione (**6e**) (1 mmol) in benzene (70 mL) containing the corresponding alcohols (5 mL) was irradiated under the same conditions for 5 h. After removal of the solvent, the residue was chromatographed with toluene/ethyl acetate (50:1) to yield benzothiazoline-2-thione (**2**) and the corresponding esters (**16**).

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