PREPARATION OF FUSED THIADIAZOLO- AND IMIDAZO-BENZOTHIAZOLES FROM 2-AMINOBENZOTHIAZOLES. THEIR FUNGICIDAL ACTIVITY

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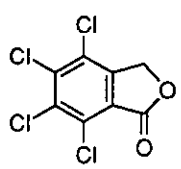
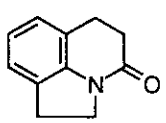
Abstract - A regioselective [2+3] cyclocondensation between chlorocarbonylsulfenyl chloride (**3**) and 2-aminobenzothiazoles gave 3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-ones (**1**). Some heterocycles (**1**) and their isosteric known 5-substituted 2-methyl-imidazo[2,1-*b*]benzothiazoles (**2**) which were prepared from 2-amino-benzothiazoles *via* two steps, showed significant fungicidal activities.

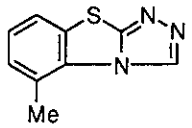
There has been considerable interest in fungicides which inhibit biosynthetic pathway for melanin,[1] because of its potent activity against rice blast disease caused by *Pyricularia oryzae*. Fthalide,[2] pyroquilon,[3] tricyclazole,[4] and chlobenthiazone[5] are the representative pesticides and some of them are now practically used for the protection of rice plant from such serious disease.



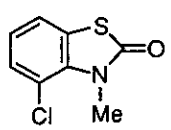
Fthalide



Pyroquilon



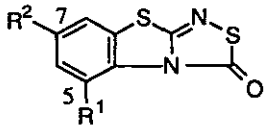
Tricyclazole



Chlobenthiazone

These compounds are basically composed of the benzolog-heterocyclic structure, and particularly, tricyclazole and chlobenthiazone have the common benzothiazole prototype. Taking this information into

with our continuing synthetic studies on *S*, *N*-containing heterocycles[6] and on biologically active compounds,[7] we report here preparations of heterocycles, 3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-ones (**1**) and 2-methylimidazo[2,1-*b*]benzothiazoles (**2**) and evaluation of their fungicidal activities.



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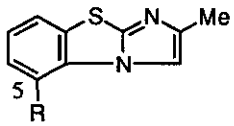


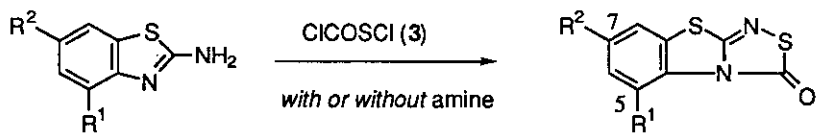
2

First, we prepared a fused heterocycle (**1**) by utilizing [2+3] cyclocondensation between chlorocarbonylsulfenyl chloride (ClCOSCl; abbreviated CCSC; **3**) and 2-aminobenzothiazoles (Table 1). CCSC (**3**) is an electrophilic bifunctional reagent which provides various heterocycles possessing -COS- linkage.[8] Many types of cyclocondensations using CCSC (**3**) were reported,[8] but they sometimes meet with serious problem of the regioselectivity.

In an α-amino-*N*-heterocyclic system, there are just two patterns for the regioselective cyclization. Extensive studies by Pilgram[9] and Broek[10] reveal that the regioselectivity depends on the reaction conditions, for example, the exocyclic α-amino group in 2-aminothiazoles condenses with carbonyl part of **3** in THF, and that condenses with the sulfenyl part of **3** in $CHCl_3$ (*vice versa*). In contrast, treatment of 2-aminobenzothiazoles with CCSC (**3**) was found to give 3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-ones (**1**) with high regioselectivity in every conditions we examined, namely, the regioisomer, 2*H*-1,2,4-thiadiazolo[3,2-*b*]benzothiazol-3-ones were not detected. The reason for this regioselectivity is not clear presently, but along with Broek's speculation,[10] we suppose that inherently reactive *exo*-amino group in 2-aminobenzothiazoles[11] first bonds with the sulfenyl part of **3** during the kinetically controlled cyclocondensation. It is also noted that the yield was better in the absence of amine (Table 1, entries 2-4), although this condition was not examined so far for 2-aminothiazole-type substrates. The structures of **1** were determined by ^1H NMR, ^{13}C NMR, IR spectra, elementary analyses, and unambiguously confirmed by X-Ray crystallography of compound (**1b**) (Figure 1).

Next, we prepared 2-methylimidazo[2,1-*b*]benzothiazoles (**2**) as an isoster of tricyclazole and **1**. Synthesis of the heterocycle (**2**) was reported;[12] couplings of 2-aminobenzothiazoles with 2-propynyl bromide give 2-amino-3-(2-propynyl)benzothiazoles **4**, which are converted into **2** by cyclocondensation using NaOH. For the first coupling step, we use 2,3-dichloropropene in the place of 2-propynyl bromide which possesses explosive characteristics.[13] The following cyclization step was carried out in H_2SO_4 or by

Table 1. [2+3] Cyclocondensation of CCSC (3) with 2-Aminobenzothiazoles.[a]



1

entry	R^1	R^2	amine	solvent	product	yield / %
1	H	H	none	1,2-dichloroethane	**1a**	18
2	H	H	none	toluene	**1a**	38
3	H	H	Et_3N	toluene	**1a**	11
4	H	H	Bu_3N	toluene	**1a**	25
5	Me	H	none	toluene	**1b**	22
6	H	Me	none	toluene	**1c**	40
7	H	Cl	none	toluene	**1d**	15
8	H	MeO	none	toluene	**1e**	29

[a] The reactions were carried out at 100-110 °C for 5 h without amines or 0 °C-rt with amines for 10 h. Molar ratio of **3** : 2-aminobenzothiazole : (amine) = 1.1 : 1.0 : (1.1).

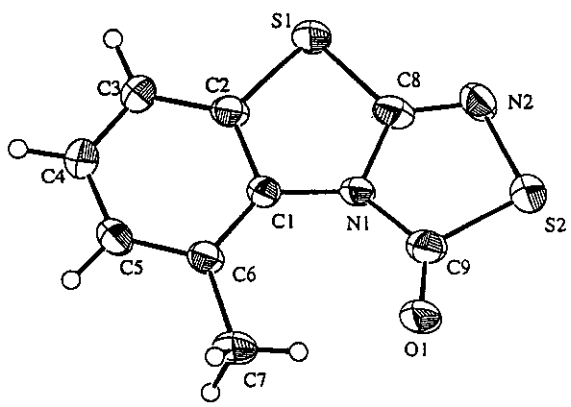
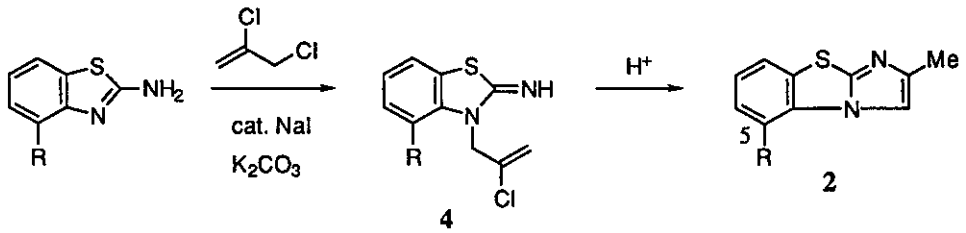


Figure 1 X-Ray structure of 5-methyl-3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-one (**1b**).

using $Hg(OCOCF_3)_2$.[14]

Taking into consideration the fungicidal SAR (structure-activity relationship) of **1** (*vide infra*), we prepared new analogs (**2b**) and (c) bearing methyl group and chlorine, respectively, at their 5-position. ^1H NMR, ^{13}C NMR, IR, MS spectra and elementary analyses rationally supported the structure of **2**.



4 2

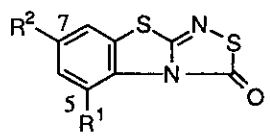
Finally, we describe the SAR of these compounds (**1**) and (**2**). The fungicidal activities against *Pyricularia oryzae*, *Rhizoctonia solani*, *Sphaerotheca fuliginea*, and *Pseudocerosporella herpotrichoides* were assessed. Table 2 lists these results.

As we expected, methyl substituted compounds **1b** and **1c** showed significant fungicidal activity against *P. oryzae*. at 500 ppm. They have also mild activity against *R. solani*. Compounds (**2a-c**) also showed significant activity against *P. oryzae* at 500 ppm. However, these activities are lower than those of tricyclazole and chlobenthiazone. It is worth noting that chlorine-containing compound (**2c**) possessed wide spectrum for *P. oryzae*, *S. fuliginea*, and *P. herpotrichoides*. All these results indicate that a substituent at the 5-position in **1** and **2** effects the fungicidal activities. This tendency coincides with the known melanin-biosynthesis-inhibiting fungicides.

EXPERIMENTAL

All melting points were determined on a hot stage microscope apparatus (Yanagimoto) and are uncorrected. ^1H NMR spectra were recorded on a JEOL EX-90 (90 MHz) or a JEOL α (400 MHz) spectrometers using TMS as an internal standard in $CDCl_3$. ^{13}C NMR spectra were recorded on a JEOL α spectrometer (100 MHz) using TMS as an internal standard in $CDCl_3$. MS spectra were obtained on a Hitachi M-80 spectrometer. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. Silica gel column chromatography was performed on a Merck Art. 7734. 2-Aminobenzothiazoles are commercially available.

Table 2 Fungicidal activity of compounds (1) and (2)[a]



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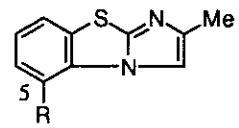

2

Compound	R^1	R^2	R	Activity ratings[b]			
				Pyricularia oryzae	*Rhizoctonia solani*	*Sphaerotheca fuliginea*	*Pseudocerosporella herpotrichoides*
1a	H	H	--	4	2	0	0
1b	Me	H	--	5	4	0	0
1c	H	Me	--	5	2	0	0
1d	H	Cl	--	1	0	0	0
1e	H	MeO	--	0	0	0	0
2a	--	--	H	4	0	0	0
2b	--	--	Me	3	0	0	0
2c	--	--	Cl	5	0	5	4

[a] The fungicidal activity was determined according to the reported method.[15]

[b] 500 ppm: 1, below 50% controlled *vs.* untreated; 2, 50-69%; 3, 70-89%; 4, 90-99%; 5, 100%.

Typical procedure of preparing 5-methyl-3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-one (1b).

CCSC (**3**, 144 mg, 1.1 mmol) was added to a stirred suspension of 2-amino-4-methylbenzothiazole (164 mg,1.0 mmol) in toluene (4.0 mL) at 0-5 °C. The mixture was heated at 100-110 °C for 5 h, and then being cooled down, diluted with EtOAc, filtered through Celite using EtOAc. The organic phase was separated, washed with water and brine, dried (Na_2SO_4), concentrated. The crude residue was purified by silica gel column chromatography (hexane/ethyl acetate = 3:1) to give the desired compound (84 mg, 38 %). Orange colored crystals (2-propanol), mp 131.5-133.5 °C; Anal. Calcd for $C_9H_6N_2OS_2$: C, 48.63; H, 2.72; N, 12.60. Found C, 48.33; H, 2.56; N, 12.24. ^{1}H NMR δ = 2.85 (3H, s), 7.17-7.29 (3H, m); ^{13}C NMR δ = 23.36, 120.99, 127.04, 127.05, 128.48, 130.93, 131.12, 155.17, 173.04; IR (film) ν_{max}: 3449, 1711, 1314, 1271, 1233 cm^{-1}.

X-Ray Crystallography of 1b.

Intensity data were collected on a Rigaku AFC7R diffractometer using graphite-monochromated CuKα radiation (λ=1.54178 Å). Crystal data are as follows: $C_9H_6N_2S_2O$, *M* 222.28, monoclinic, space group $P2_1/n$, a = 7.867(6) Å, b = 12.950(6) Å, c = 9.190(6) Å, β = 103.12(6)°, V = 911(1) Å^3, Z = 4, F(000) = 456.00, D_X = 1.619 gcm^{-3}, μ(CuKα) = 50.01 cm^{-1}. A total of 1633 reflections up to a maximum 2θ of 130° were collected by ω-2θ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares. Non-hydrogen atoms were refined with anisotropic thermal parameters. The final R and Rw factors were 0.071 and 0.095, respectively, for 1199 observed reflections [I>3σ (I)]. All calculations were carried out on an Indigo^2 workstation using teXan package. Bond distances, bond angles, torsional angles, final positional parameters, anisotropic thermal parameters are available on any current masthead page.

3*H*-1,2,4-Thiadiazolo[3,4-*b*]benzothiazol-3-one (1a).

Light red colored crystals (2-propanol), mp 149.0-150.0 °C; Anal. Calcd for $C_8H_4N_2OS_2$: C, 46.14; H, 1.94; N, 13.45. Found C, 46.03; H, 1.88; N, 13.11. ^{1}H NMR δ = 7.36-7.46 (2H, m), 7.50-7.52 (1H, m), 8.21-8.23 (1H, m); ^{13}C NMR δ = 114.46, 123.33, 126.67, 127.10, 127.77, 130.90, 154.21, 172.84; IR (film) ν_{max} 1705, 1684, 1346, 1304, 1238 cm^{-1}. The reactions using amine catalysts are as follows. CCSC (**3**, 144 mg, 1.1 mmol) was added to a stirred suspension of 2-aminobenzothiazole (150 mg, 1.0 mmol) and Et3N (111 mg, 1.1 mmol) in toluene (4.0 mL) at 0-5 °C. The mixture was stirred at rt for 10 h. Following a similar work up for preparing **1b** described above, **1a** (23 mg, 11%) was obtained. Use of Bu3N (204 mg, 1.1 mmol) in the place of Et3N gave **1a** (52 mg, 25%).

7-Methyl-3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-one (1c).

Light brown colored crystals (2-propanol), mp 164.0-165.5 °C; Anal. Calcd for $C_9H_6N_2OS_2$: C, 48.63; H, 2.72; N, 12.60. Found C, 48.45; H, 2.67; N, 12.44. ^{1}H NMR δ = 2.43 (3H, s), 7.20-7.29 (2H, m), 8.04-8.06 (1H, m); ^{13}C NMR δ = 21.40, 114.03, 123.44, 127.68, 127.84, 128.64, 137.01, 154.39, 172.71; IR (film) ν_{max} 3441, 1698, 1545, 1302, 1250 cm^{-1}.

7-Chloro-3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-one (1d).

Light yellow colored crystals (2-propanol), mp 178.0-180.0 °C; Anal. Calcd for $C_8H_3ClN_2OS_2$: C, 39.59; H, 1.25; N, 14.61. Found C, 39.37; H, 1.18; N, 14.44. ^{1}H NMR δ = 7.40-7.43 (1H, m), 7.48-7.52 (1H, m), 8.13-8.16 (1H, m); ^{13}C NMR δ = 115.21, 123.21, 127.48, 129.40, 132.34, 153.46, 172.56; IR (film) ν_{max} 3449, 1701, 1678, 1545, 1298 cm^{-1}.

7-Methoxy-3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-one (1e).

Light brown colored crystals (2-propanol), mp 157.0-159.0 °C; Anal. Calcd for $C_9H_6N_2O_2S_2$: C, 45.36; H, 2.54; N, 11.76. Found C, 45.11; H, 2.38; N, 11.52. ^{1}H NMR δ = 3.86 (3H, s), 6.93-6.96 (1H, m), 7.01-7.02 (1H, m), 8.08-8.11 (1H, m); ^{13}C NMR δ = 55.85, 108.54, 112.99,115.17, 124.69, 129.15, 154,22, 158.24, 172.56; IR (film) ν_{max} 3441, 1711, 1545, 1290, 1217 cm^{-1}.

3-(2-chloro-2-propenyl)-2,3-dihydro-2-imino-4-methylbenzothiazole (4b).

2,3-Dichloropropene (3.72 g, 33.5 mmol) was added to a stirred suspension of 2-amino-4-methylbenzothiazole (5.00 g, 30.4 mmol), K_2CO_3 (4.63 g, 33.5 mmol), and NaI (0.91 g, 6.1 mmol) in DMF (30.0 mL) at rt and the mixture was heated at 110-120 °C for 10 h and being cooled down. Water was added to the mixture, which was extracted with EtOAc. The organic phase was washed with water and brine, dried (Na_2SO_4), and concentrated. The crude residue was purified by silica gel column chromatography (hexane/ethyl acetate = 9:1) to give the desired compound (2.11 g, 29%). Light yellow colored crystals (2-propanol), mp 90.5-92.5 °C; Anal. Calcd for $C_{11}H_{11}ClN_2S$: C, 55.34; H, 4.64; N, 11.73. Found C, 55.12; H, 4.37; N, 11.44. ^{1}H NMR δ = 2.56 (3H, s), 4.19 (2H, s), 5.36-5.37 (1H, m), 5.52-5.53 (1H, m), 6.13 (1H, br s), 7.00-7.45 (3H, m); ^{13}C NMR δ = 18.33, 51.21, 113.83, 118.32, 121.83, 126.81, 129.06, 130.26, 137.66, 151.05, 166.04; IR (film) ν_{max} 3219, 1616, 1570, 1321, 1217 cm^{-1}.

3-(2-Chloro-2-propenyl)-2,3-dihydro-2-iminobenzothiazole (4a).

A similar procedure as that for preparing **4b** gave the desired compound in 32% yield. Light colored crystals (2-propanol), mp 149-150 °C; Anal. Calcd for $C_{10}H_9ClN_2S$: C, 53.45; H, 4.04; N, 12.47. Found C, 53.23; H, 3.99; N, 12.24. ^{1}H NMR δ = 4.24 (2H, s), 5.39-5.40 (1H, m), 5.54-5.55 (1H, m), 7.10-7.61 (4H, m); ^{13}C NMR δ = 50.98, 113.92, 119.22, 120.89, 122.04, 126.08, 137.61, 151.91, 166.77; IR (film) ν_{max} 3164, 1645, 1622, 1520, 1094 cm^{-1}.

4-Chloro-3-(2-chloro-2-propenyl)-2,3-*dihydro*-2-iminobenzothiazole (4c).

A similar procedure as that for preparing **4b** gave the desired compound in 18% yield. Yellow colored crystals (2-propanol), mp 104.0-106.0 °C; Anal. Calcd for $C_{10}H_8Cl_2N_2S$: C, 46.35; H, 3.11; N, 10.81. Found C, 46.10; H, 3.02; N, 10.66. ^{1}H NMR δ = 4.19 (2H, s), 5.35-5.37 (1H, m), 5.52-5.53 (1H, m), 7.00-7.51 (3H, m), 7.93 (1H, br s); ^{13}C NMR δ = 51.73, 113.67, 119.44, 122.13, 123.15, 126.31, 131.21, 137.07, 148.89, 168.81; IR (film) ν_{max} 3449, 1615, 1568, 1219, 1090 cm^{-1}.

2,5-Dimethylimidazo[2,1-*b*]benzothiazoles (2b).

A mixture of 3-(2-chloro-2-propenyl)-2,3-dihydro-2-imino-4-methylbenzothiazole (**4b**; 0.88 g, 3.7 mmol) in conc. H_2SO_4 (10 mL) was allowed to stand at rt for 10 h. The mixture was diluted with water and

brine, dried (Na_2SO_4), and concentrated. The crude residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to give the desired compound (0.15 g, 20%). Yellow colored crystals (2-propanol), mp 123.0-126.0 °C; Anal. Calcd for $C_{11}H_{10}N_2S$: C, 65.32; H, 4.98; N, 13.85. Found C, 65.16; H, 4.88; N, 13.71. ^{1}H NMR δ = 2.69 (3H, s), 2.76 (3H, s), 7.03-7.04 (1H, m), 7.15-7.21 (2H, m), 7.47-7.50 (1H, m); ^{13}C NMR δ = 15.59, 23.66, 122.13, 123.66, 124.00, 124.38, 129.41, 130.95, 133.50, 134.21, 148.54; IR (film) ν_{max} 3441, 1491, 1339, 1233, 1148 cm^{-1};MS (70 eV) *m/z* 202 (M^+, 95), 201 (M^+-1, 100). Product (**2b**) was also obtained by use of 1.1 equiv of $Hg(OCOCF_3)_2$ in refluxing CF_3CO_2H solvent in 19% yield.

2-Methylimidazo[2,1-*b*]benzothiazoles (2a).[12a]

A similar procedure as that for preparing **2b** gave the desired compound in 20% yield. Red colored oil; ^{1}H NMR δ = 2.69 (3H, s), 7.18-7.50 (3H, m), 7.65-7.82 (1H, m); ^{13}C NMR δ = 14.66, 108.17, 112.34, 112.57, 124.23, 124.33, 125.81, 125.98, 131.81, 147.56; IR (film) ν_{max} 3441, 1491, 1339, 1233, 1148 cm^{-1}; ms *m/z* 188 (M^+, 95), 187 (M^+-1, 100).

5-Chloro-2-methylimidazo[2,1-*b*]benzothiazoles (2c).

A similar procedure as that for preparing **2b** gave the desired compound in 15% yield. Light yellow colored crystals (2-propanol), mp 124.0-125.0 °C; Anal. Calcd for $C_{10}H_7ClN_2S$: C, 53.93; H, 3.17; N, 12.58. Found C, 53.84; H, 3.12; N, 12.43. ^{1}H NMR δ = 2.81 (3H, s), 7.05 (1H, brs), 7.18-7.50 (3H, m); ^{13}C NMR δ = 16.31, 118.60, 122.80, 125.06, 125.84, 128.42, 131.64, 132.81, 133.76, 147.89; IR (film) ν_{max} 3426, 1493, 1246, 1194, 1146 cm^{-1}.

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REFERENCES AND NOTES

1. a) I. Shimazaki, 'Bioorganic Chemistry of Pesticide - Research and Development,' ed. by M. Eto, Soft Science, Inc., Tokyo, 1985, chap. 2, p. 68 (in Japanese); b) N. Ohno, S. Inoue, and H. Yoshioka, *Kagaku no Ryoiki*, 1983, **37**, 516 (in Japanese); e) R. D. Stipanovic and A. A. Bell, *J. Org. Chem.*, 1976, **41**, 2468; d) C. P. Woloshunk and H. D. Sisler, *J. Pesticide Sci.*, 1982, **7**, 161.

2. T. Chida, T. Uekita, K. Satake, K. Hirano, K. Aoki, and T. Noguchi, *Ann. Phytopathol. Soc. Jpn.*, 1982, **48**, 58 (in Japanese).
3. F. Schwinn, M. Nakamura, and G. Handshin, *9th International Congress of Plant Protection*, 1979, 479.
4 a) J. D. Froyd, C. J. Paget, L. R. Guse, B. A. Dreikorn, and J. L. Pafford, *Phytopathology*, 1976, **66**, 1135; b) M. C. Tokousbalides, and S. R. Dutky, *Pestic. Biochem. Physiol.*, 1987, **8**, 26; c) C. P. Woloshunk, H. D. Sisler, M. C. Tokousbalides, and S. R. Dutky, *Pestic. Biochem. Physiol.*, 1987, **8**, 26; d) C. P. Woloshunk, P. M. Wolkow, and H. D. Sisler, *Pestic. Sci.*, 1981, **12**, 86.
5. T. Uematsu, S. Inoue, and N. Yamashita, *Ger. Offen.*, 1978, 2801868 (*Chem. Abstr.*, 1978, **89**, 179989s).
6. For recent studies: a) Y. Sanemitsu, S. Kawamura, and Y. Tanabe, *J. Org. Chem.*, 1992, **57**, 1053; b) Y. Tanabe, T. Makita, and K. Mori, *Chem. Lett.*, 1994, 2275; c) Y. Tanabe, H. Yamamoto, M. Murakami, K. Yanagi, Y. Kubota, H. Okumura, Y. Sanemitsu, and G. Suzukamo, *J. Chem. Soc., Perkin Trans. 1*, 1995, 935; d) Y. Tanabe, H. Okumura, M. Nagaosa, and M. Murakami, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1467; e) Y. Tanabe, M. Nagaosa, and Y. Nishii, *Heterocycles*, 1995, **41**, 2033; f) Y. Tanabe, K. Mori, and Y. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1997, 671.
7. For recent studies: a) Y. Tanabe, G. Suzukamo, Y. Komuro, N. Imanishi, S. Morooka, M. Enomoto, A. Kojima, Y. Sanemitsu, and M. Mizutani, *Tetrahedron Lett.*, 1991, **32**, 379; b) Y. Nishii, H. Matsumura, Y. Muroya, T. Tsuchiya, and Y. Tanabe, *Biosci. Biotech. Biochem.*, 1995, **59**, 1355; c) Y. Nishii, K. Wakimura, T. Tsuchiya, S. Nakamura, and Y. Tanabe, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1243; d) Y. Tanabe, S. Seko, Y. Nishii, T. Yoshida, N. Utsumi, and G. Suzukamo, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2157; e) Y. Nishii, K. Watanabe, T. Yoshida, T. Okayama, S. Takahashi, and Y. Tanabe, *Tetrahedron*, 1997, **53**, 7209.
8. a) V. G. Zumach and E. Kuhle, *Angew. Chem., Int. Ed. Engl.*, 1970, **82**, 63; b) E. Muehlbauer and W. Weiss, German Pat. 1233882 (*Chem. Abstr.*, 1967, **66**, 95023j); c) R. K. Howe, T. A. Gruner, and J. E. Franz, *J. Org. Chem.*, 1977, **42**, 1813; d) C. H. Xi and G. Kollenz, *Heterocycles*, 1992, **34**, 2293; e) J. N. Bridson, M. J. Schriver, and S. Zhu, *Can. J. Chem.*, 1995, **73**, 212; f) L. Chen, T. R. Thompson, R. P. Hammer, and G. Barany, *J. Org. Chem.*, 1996, **61**, 6639; g) Y. Tanabe, K. Mori, and Y. Nishii, *Heterocycles*, 1996, **43**, 141. Other recent studies cited therein. CCSC (**3**) is commercially available and is also prepared from Cl_3CSCl and 95 % H_2SO_4-H_2O in a large scale.
9. K. Pilgram and R. D. Skiles, *J. Org. Chem.*, 1973, **38**, 1578;
10. D. Baldwin and P. Van den Broek, *J. Chem. Soc., Perkin Trans. 1*, 1975, 375;
11. P. Merino, 'Comprehensive Heterocyclic Chemistry II,' ed. by A. Katritzky, Pergamon, Oxford, 1996, Vol. 3, p. 412.
12. a) I. Iwai and T. Hiraoka, *Chem. Pharm. Bull.*, 1964, **12**, 813; b) H. Ogura, T. Itoh, O. Haruo,

Chem. Pharm. Bull., 1970, **18**, 1981; c) A. N. Krasovskii, N. P. Grin, I. I. Soroka, P. M. Kochergin, and E. I. Bogatyreva, *Khim. -Farm. Zh.*, 1977, **11**, 25 (*Chem. Abstr.*, 1977, **87**, 201412f). This paper describes some analogs of **2** possess mild fungicidal activity, but there is no data. d) N. Abe and T. Nishiwaki, *Heterocycles*, 1981, **16**, 537; e) N. Abe and T. Nishiwaki, T. Omori, and E. Harada, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 200; f) T. Seki, S. Tasaka, and R. Hoshino, Eur. Pat., 1989, 347880 (*Chem. Abstr.*, 1990, **113**, 23910n). This patent claims some analogs of **2** as an antiulcer agent.

13. Y. Tanabe, H. Yamamoto, Y. Yoshida, T. Miyawaki, and N. Utsumi, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 297.
14. For related reactions: (a) L. E. Fieser and M. Fieser, 'Reagent for Organic Synthesis,' Wiley, New York, 1967, Vol. I, p. 214; (b) T. Mukaiyama, T. Imamoto, and S. Kobayashi, *Chem. Lett.*, **1973**, 261; (c) F. S. Martin and T. Chou, *Tetrahedron Lett.*, **1978**, 1943; (d) Y. Tanabe, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3309.
15. H. Takano, Y. Oguri, and T. Kato, *J. Pesticide Sci.*, 1982, **11**, 373.

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