

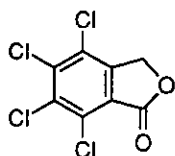
**PREPARATION OF FUSED THIADIAZOLO- AND IMIDAZO-
BENZOTHAZOLES FROM 2-AMINOBENZOTHAZOLES.
THEIR FUNGICIDAL ACTIVITY**

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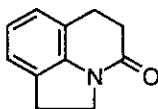
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Abstract - A regioselective [2+3] cyclocondensation between chlorocarbonylsulfenyl chloride (**3**) and 2-aminobenzothiazoles gave 3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-ones (**1**). Some heterocycles (**1**) and their isosteric known 5-substituted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

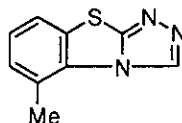
There has been considerable interest in fungicides which inhibit biosynthetic pathway for melanin,¹ because of its potent activity against rice blast disease caused by *Pyricularia oryzae*. Fthalide,² pyroquilon,³ tricyclazole,⁴ and chlobenthiazone⁵ are the representative pesticides and some of them are now practically used for the protection of rice plant from such serious disease.



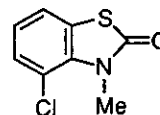
Fthalide



Pyroquilon



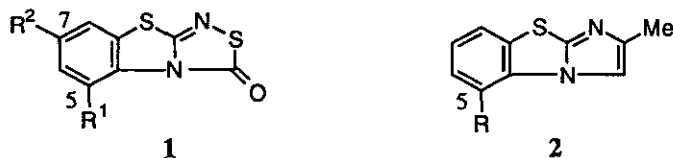
Tricyclazole



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

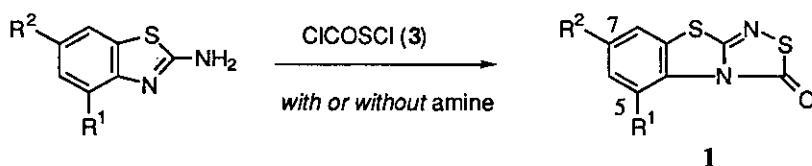
with our continuing synthetic studies on *S*, *N*-containing heterocycles⁶ and on biologically active compounds,⁷ we report here preparations of heterocycles, 3*H*-1,2,4-thiadiazolo[3,4-*b*]benzothiazol-3-ones (1) and 2-methylimidazo[2,1-*b*]benzothiazoles (2) and evaluation of their fungicidal activities.



First, we prepared a fused heterocycle (1) by utilizing [2+3] cyclocondensation between chlorocarbonylsulfonyl 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 Pilgram⁹ and Broek¹⁰ 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 sulfonyl part of 3 in CHCl₃ (*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-aminobenzothiazoles¹¹ first bonds with the sulfonyl 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, ¹³C 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 H₂SO₄ or by

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

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 ₃ N	toluene	1a	11
4	H	H	Bu ₃ N	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).

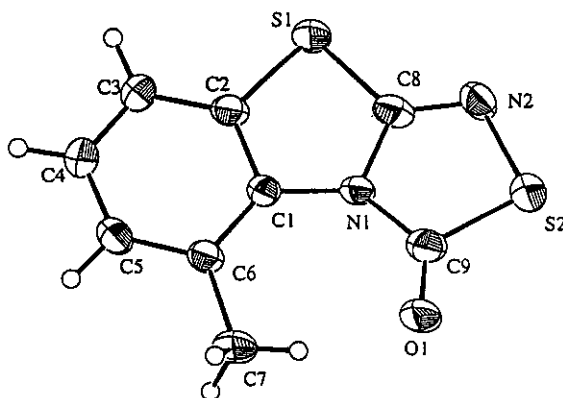
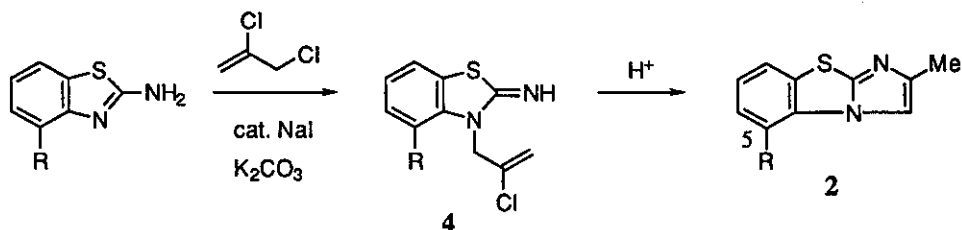


Figure 1 X-Ray structure of 5-methyl-3H-1,2,4-thiadiazolo[3,4-b]benzothiazol-3-one (**1b**).

using $\text{Hg}(\text{OCOCF}_3)_2$.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**.

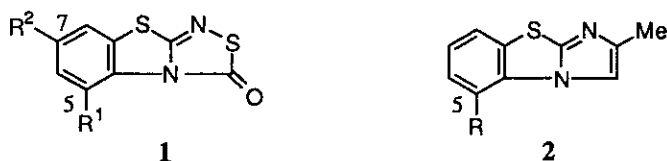


Finally, we describe the SAR of these compounds (**1**) and (**2**). The fungicidal activities against *Pyricularia oryzae*, *Rhizoctonia solani*, *Sphaerotheca fuliginea*, and *Pseudocerospora herpotrichoides* were assessed. Table 2 lists these results.

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 chlobenthiazole. 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

Compound	R ¹	R ²	R	Activity ratings ^b			
				<i>Pyricularia oryzae</i>	<i>Rhizoctonia solani</i>	<i>Sphaerotheca fuliginea</i>	<i>Pseudocerosporella herpotrichoides</i>
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-3H-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 (Na₂SO₄), 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 C₉H₆N₂OS₂: C, 48.63; H, 2.72; N, 12.60. Found C, 48.33; H, 2.56; N, 12.24. ¹H NMR δ = 2.85 (3H, s), 7.17-7.29 (3H, m); ¹³C 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 $\text{CuK}\alpha$ radiation ($\lambda=1.54178 \text{ \AA}$). Crystal data are as follows: $\text{C}_9\text{H}_6\text{N}_2\text{S}_2\text{O}$, M 222.28, monoclinic, space group $\text{P}2_1/\text{n}$, $a = 7.867(6) \text{ \AA}$, $b = 12.950(6) \text{ \AA}$, $c = 9.190(6) \text{ \AA}$, $\beta = 103.12(6)^\circ$, $V = 911(1) \text{ \AA}^3$, $Z = 4$, $F(000) = 456.00$, $D_x = 1.619 \text{ g cm}^{-3}$, $\mu(\text{CuK}\alpha) = 50.01 \text{ cm}^{-1}$. 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 R_w factors were 0.071 and 0.095, respectively, for 1199 observed reflections [$I > 3\sigma(I)$]. All calculations were carried out on an Indigo² workstation using *teXan* package. Bond distances, bond angles, torsional angles, final positional parameters, anisotropic thermal parameters are available on any current masthead page.

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

Light red colored crystals (2-propanol), mp $149.0\text{--}150.0^\circ\text{C}$; Anal. Calcd for $\text{C}_8\text{H}_4\text{N}_2\text{OS}_2$: C, 46.14; H, 1.94; N, 13.45. Found C, 46.03; H, 1.88; N, 13.11. ^1H NMR $\delta = 7.36\text{--}7.46$ (2H, m), $7.50\text{--}7.52$ (1H, m), $8.21\text{--}8.23$ (1H, m); ^{13}C NMR $\delta = 114.46, 123.33, 126.67, 127.10, 127.77, 130.90, 154.21, 172.84$; IR (film) $\nu_{\text{max}} 1705, 1684, 1346, 1304, 1238 \text{ cm}^{-1}$. 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 Et_3N (111 mg, 1.1 mmol) in toluene (4.0 mL) at $0\text{--}5^\circ\text{C}$. 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 Bu_3N (204 mg, 1.1 mmol) in the place of Et_3N gave **1a** (52 mg, 25%).

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

Light brown colored crystals (2-propanol), mp $164.0\text{--}165.5^\circ\text{C}$; Anal. Calcd for $\text{C}_9\text{H}_6\text{N}_2\text{OS}_2$: C, 48.63; H, 2.72; N, 12.60. Found C, 48.45; H, 2.67; N, 12.44. ^1H NMR $\delta = 2.43$ (3H, s), $7.20\text{--}7.29$ (2H, m), $8.04\text{--}8.06$ (1H, m); ^{13}C NMR $\delta = 21.40, 114.03, 123.44, 127.68, 127.84, 128.64, 137.01, 154.39, 172.71$; IR (film) $\nu_{\text{max}} 3441, 1698, 1545, 1302, 1250 \text{ cm}^{-1}$.

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

Light yellow colored crystals (2-propanol), mp $178.0\text{--}180.0^\circ\text{C}$; Anal. Calcd for $\text{C}_8\text{H}_3\text{ClN}_2\text{OS}_2$: C, 39.59; H, 1.25; N, 14.61. Found C, 39.37; H, 1.18; N, 14.44. ^1H NMR $\delta = 7.40\text{--}7.43$ (1H, m), $7.48\text{--}7.52$ (1H, m), $8.13\text{--}8.16$ (1H, m); ^{13}C NMR $\delta = 115.21, 123.21, 127.48, 129.40, 132.34, 153.46, 172.56$; IR (film) $\nu_{\text{max}} 3449, 1701, 1678, 1545, 1298 \text{ cm}^{-1}$.

7-Methoxy-3H-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. 1H 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. 1H 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. 1H 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. 1H 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 $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}$: C, 65.32; H, 4.98; N, 13.85. Found C, 65.16; H, 4.88; N, 13.71. ^1H 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 $\text{Hg}(\text{OCOCF}_3)_2$ in refluxing $\text{CF}_3\text{CO}_2\text{H}$ 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; ^1H 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 $\text{C}_{10}\text{H}_7\text{ClN}_2\text{S}$: C, 53.93; H, 3.17; N, 12.58. Found C, 53.84; H, 3.12; N, 12.43. ^1H 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); c) 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. I*, 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. I*, 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. I*, 1996, 1243; d) Y. Tanabe, S. Seko, Y. Nishii, T. Yoshida, N. Utsumi, and G. Suzukamo, *J. Chem. Soc., Perkin Trans. I*, 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 Cl₃CSCl and 95 % H₂SO₄-H₂O 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. I*, 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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