REGIOCONTROLLED CARBONYLSULFANYLATIONS AT *ORTHO*-POSITION OF PHENOLS AND AT α-POSITION OF KETONES USING CHLOROCARBONYLSULFENYL CHLORIDE

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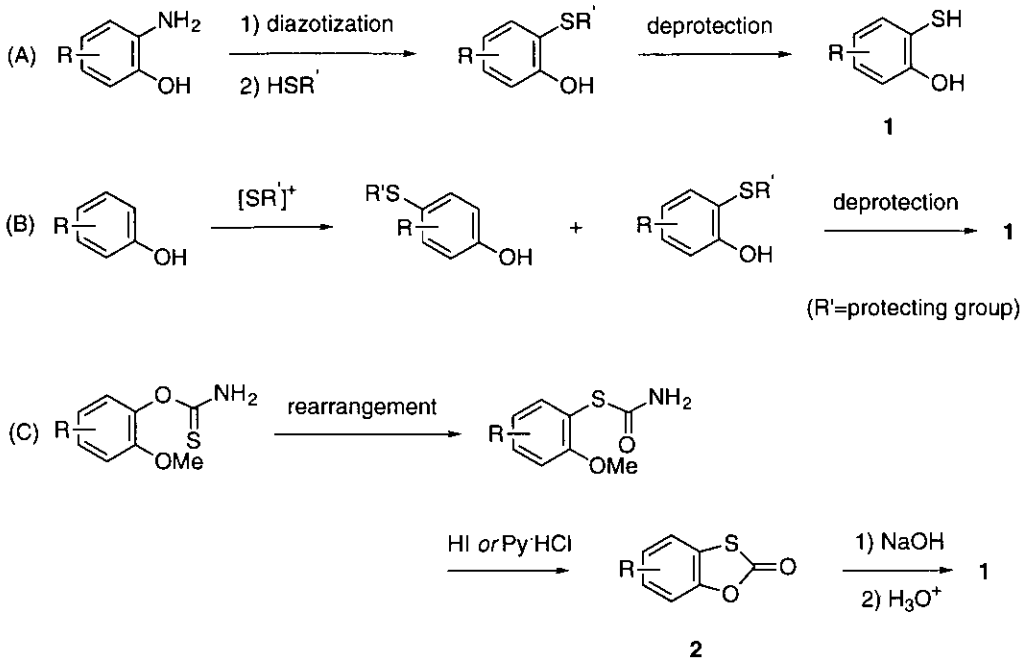
Abstract - $Bu_3N/AlCl_3$-promoted [3+2] cyclocondensation between phenols and chlorocarbonylsulfenyl chloride (CCSC; **3**) gave 1,3-benzoxathiol-2-ones (**2**), wherein the acylation of phenols with CCSC (**3**) and the intramolecular and regioselective *ortho*-sulfenylation successively proceeded in a one-pot manner. 2-Sulfanylphenols (**1**) were produced from **2** by mild hydrolysis using NaOH. An analogous Bu_3N-promoted [3+2] cyclocondensation between ketones and **3** gave 1,3-oxathioles (**7**), wherein the α-CH_2- position of the ketones was regioselectively sulfenylated.

2-Sulfanyl(mercapto)phenols are representative sulfur-containing isosters for catecohols. Some of the substituted 2-sulfanylphenols (**1**) are useful for heat stabilizers,[1] and serve as ligands for several metals (B, Zn, Cd, Mo, Pb, etc.)[2] and as useful precursors for sulfur-containing heterocycles; 1,5-benzoxathiepin-type drugs[3,4] and benzonaphtho-1,4-dithiin-type organic semiconductors.[5]

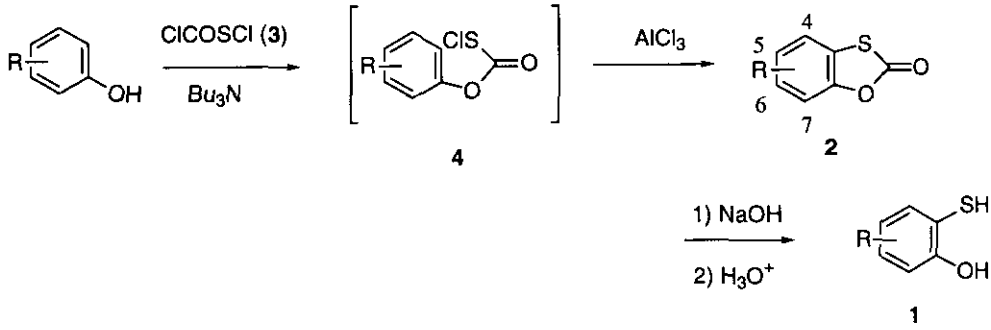
As illustrated in Scheme 1, there have been a few general methods A, B, and C already employed for the preparation of **1**. However, regarding method A,[6] the availability of substituted *ortho*-aminophenols is limited. Method B[6] has a serious drawback in controlling the orientation; the sulfanyl moiety is more predominantly introduced into the *para*-position than into the *ortho*-position of the starting phenols. Although method C[7] has a merit that hydrolysis of **2** easily proceed under mild conditions, the preparation of **2** often requires multistep procedure.[8]



Scheme 1

Regiocontrolled introduction of a sulfanyl group at the *ortho*-position of phenols is, therefore, considered to be a worthwhile and straightforward way for preparing some types of 2-sulfanylphenols (**1**). During our continuing synthetic studies on the *S*, *N*-containing heterocycles,[9] we have reported several methods[10] for preparing such compounds possessing a -COS- linkage utilizing chlorocarbonylsulfenyl chloride[11] (ClCOSCl; abbreviated as CCSC; **3**). We describe here an effective method for the preparation of several 1,3-benzoxathiol-2-ones (**2**), which involves the direct and regioselective *ortho*-carbonylsulfenylation of phenols. These 1,3-benzoxathiol-2-ones (**2**) were easily converted into 2-sulfanylphenols (**1**) by mild hydrolysis. The sequenece is outlined in Scheme 2.

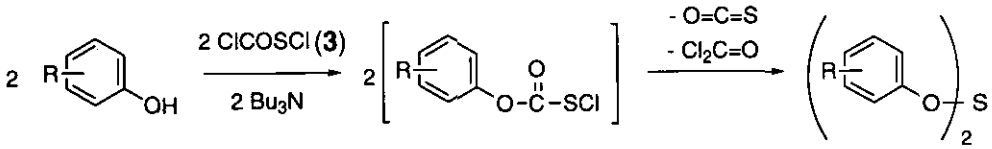
As exemplified in the reported reactions for preparing *N*-alkyl-2(3*H*)-benzothiazolones and in the related reactions,[10] CCSC (**3**) is an effective electrophilic and bifunctional reagent containing both hard carbonyl and soft sulfenyl groups in its simple molecule. Based on these studies, we planned to apply **3** to the [3+2] cyclocondensation of phenols (**1**) for preparing substituted 1,3-benzoxathiol-2-ones (**2**).



Scheme 2

Initially, we re-examined a reported cyclocondensation[12] of 2-naphthol with CCSC (**3**) to give naphth[1,2-*d*]-1,3-oxathiol-2-one (**2a**). Although the details are not described in this literature, several trials in our hands failed to obtain the desired compound in practical yields (<5%). In order to solve this problem, we screened good promoters for the cyclocondensation.

Several amine bases for the initial acylation step were examined using 2-naphthol and *p*-cresol as the substrates. The reactions were very sluggish in the case of using Et3N, pyridine, and even *N,N*-dimethylaniline which is employed for the similar cyclocondensation in the case of *N*-alkylanilines.[10a] The use of Bu3N, a milder amine-base, did not give the expected product (**2a**) and (**2d**) but resulted in the main formation of the bimolecular coupling-type product (**6a**) and (**6b**) in 19% and 31% yields, respectively (Scheme 3). We presumed that this intermolecular coupling accompanied by eliminating O=C=S and Cl_2CO predominates over the desired cyclocondensation, because of the lower reactivity for the Friedel-Crafts type sulfenylation. The structure of **6a** was elucidated using IR, ^1H- and ^{13}C-NMR spectroscopies, FDMS spectrum (M^+; 318) and elementary analyses, being unambiguously determined by a preparation of the authentic compound from 2-naphthol and SCl_2.



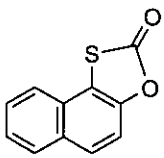
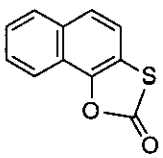
6a (from 2-naphthol)
6b (from *p*-cresol)

Scheme 3

Taking this problem into account, Lewis acid such as BF_3·OEt, $AlCl_3$, $TiCl_4$, $TiBr_4$, or $SnCl_4$ was added to the reaction system in order to activate the S-Cl bond in the intermediate (**4**). Thus, the combined

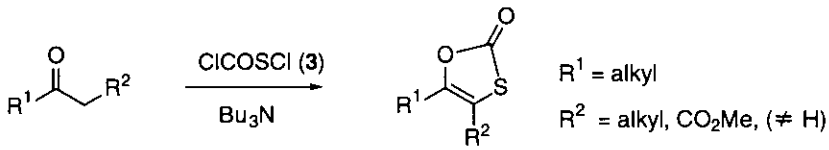
reagent, $Bu_3N/AlCl_3$[13] effectively promoted the desired cyclocondensation of phenols with CCSC (**3**) to give 1,3-benzoxathiol-2-ones (**2**) in a one-pot process (Scheme 2 and Table 1). It should be noted that hydroxyl groups in phenols apparently worked as the anchor for the *ortho*-sulfenylation step. Meanwhile, some 1,3-benzoxathiol-2-ones (**2**) are useful, because they show fungicidal activities.[14] The carbonyl linkage of **2** was easily hydrolyzed by aqueous NaOH to afford 2-sulfanyl phenols (**1**) in good yields (Table 1).

Table 1. Preparation of 1,3-Benzoxathiol-2-ones (**2**) from Phenols and CCSC (**3**). Conversion of **2** into **1** by NaOH-Hydrolysis.

Phenol (R)	1,3-Benzoxathiol-2-ones	Yield/% of **2**	2-Sulfanylphenol	Yield/% of **1**
2-Naphthol		**2a**[a] 65[b]	**1a**	70
1-Naphthol		**2b**[a] 59	**1b**	91
(H)	(H)	**2c** 63	**1c**	83
(*p*-Me)	(5-Me)	**2d** 33	**1d**	88
(*o*-Me)	(7-Me)	**2e** 31	**1e**	82
(*p*-MeO)	(5-MeO)	**2f** 48[b]	**1f**	83
(*o*-Me, *p*-Me)	(4-Me, 6-Me)	**2g** 38	**1g**	85
(*o*-Me, *p*-Cl)	(5-Cl, 7-Me)	**2h** 40	**1h**	

a) Only one regioisomer was detected. b) 2.4 Molar amounts of $AlCl_3$ were used.

To extend this cyclocondensation, we next tried the preparation of 1,3-oxathiol-2-ones (**7**) from ketones with CCSC (**3**), expecting that these carbonyl substrates behaved like phenols. Although 1,3-oxathioles are listed as a fundamental heterocycle, there are few general methods to prepare them.[15] Thus, the [3+2] cyclocondensation between ketones and **3** would become a straightforward way for preparing a 1,3-oxathiole derivative (Scheme 4).



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Scheme 4

The reaction conditions were optimized using 3-pentanone based on the results of preparing 1,3-benzoxathiol-2-ones (**2**): (a) Only trace amounts of 5-ethyl-4-methyl-1,3-oxathiol-2-one (**7a**) were obtained without any base and catalyst;[16] (b) use of Bu_3N as a base gave a 50 % yield; and (c) co-existence of $AlCl_3$ with Bu_3N decreased the yield (22%) in contrast to the case of the phenols. The results including use of other ketones are summarized in Table 2.

Table 2. Preparation of 1,3-Oxathiol-2-ones (**7**) from Ketones and CCSC (**3**).

Ketone		Product	Yield/%
R^1	R^2		of **7**
Et	Me	**7a**	50
n-Pr	Et	**7b**	50
Me	*n*-C_5H_{12}	**7c**[a)]	46
Me	CO_2Me	**7d**[a)]	54
-CH(Me)$CH_2CH_2CH_2$-		**7e**[a)]	30

a) The other diastereomer was not detected (< 5%).

It should be noted that unsymmetrically substituted ketones underwent regioselective cyclocondensation; the α-CH_2- position of unsymmetrical ketones in Table 2 was more preferentially sulfenylated than the counter α-CH_3 or the α-CH(CH_3)- position. These results indicate that the cyclocondensation proceeds through a kinetically controlled pathway, whose tendency coincides with the results of the related sulfenylations.[9c,10c,d]

In conclusion, we found straightforward methods for preparing substituted 1,3-benzoxathiol-2-ones (**2**) and oxathioles (**7**) promoted by $Bu_3N/AlCl_3$ and Bu_3N, respectively. 1,3-Benzoxathiol-2-ones (**2**) are good precursor of 2-sulfanylphenols (**1**).

EXPERIMENTAL

Melting points were determined on a hot stage microscope apparatus (Yanagimoto) and are uncorrected. ^{1}H NMR spectra were recorded on a JEOL EX-90 (90MHz) spectrometer using a TMS internal standard. ^{13}C NMR spectra (100 MHz) were recorded on a JEOL α spectrometer using a TMS internal standard. IR spectra were recorded on a JASCO FT/IR-8000 spectrophotometer. GCMS spectra were obtained with a JMS-AutoMass 50 KTR-3. Reagents were of commercial grade and were used without further purification. CCSC (**3**) was purchased from Tokyo Kasei Co. Ltd. The solvents were purified by standard methods. Silica gel column chromatography was performed on a Merck Art. 7734 and/or 9385.

Preparation of authentic bis(2-naphthyl)sulfenate (6a)

SCl_2 (1.03 g, 10.0 mmol) was added to a stirred solution of 2-naphthol (3.60 g, 25.0 mmol) and Et_3N (2.23 g, 22.0 mmol) in benzene (50 mL) at 0-5 °C. The mixture was heated to 80 °C for 13 h and poured into water (50 mL) and extracted with EtOAc. The organic layer was washed with water, brine, dried (Na_2SO_4), and concentrated to give a residue. This was purified by silica gel column chromatography (hexane/EtOAc = 3:1) and followed by recrystallization (EtOH) to give the product (135 mg, 4 %). Light yellow crystals; mp 214-217 °C; Anal. calcd for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; S, 10.7. Found: C, 75.0; H. 4.6; S, 10.3; IR (KBr) ν_{max}: 3380, 1620, 1595, 1507, 1244, 1130 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 7.17-7.19 (4H, m), 7.22-7.25 (2H, m), 7.37-7.41 (2H, m), 7.72-7.74 (4H, m), 8.52-8.54 (2H, m); ^{13}C NMR (DMSO-d_6) δ = 112.5, 118.2, 123.1, 124.7, 127.0, 128.4, 128.6, 130.5, 135.5, 156.8.

Reaction of 2-naphthol with CCSC (3) in the absence of Lewis acid catalyst:

(1) A mixture of 2-naphthol (0.72 g, 5.0 mmol) and CCSC (**3**; 0.72 g, 5.5 mmol) in toluene (10 mL) was stirred at rt for 10 h. TLC check showed that 2-naphthol did not change. Then, the mixture was heated at 110 °C for 5 h. Water was added to the mixture, which was extracted with Et_2O. The organic phase was washed with water and brine, dried (Na_2SO_4) and concentrated. The crude oil obtained was purified by silica gel column chromatography (hexane/EtOAc = 3:1) to give naphth[1,2-*d*]-1,3-oxathiol-2-one (**2a**, 78 mg, 4%) and bis(2-naphthyl)sulfenate (**6a**, 22 mg, 3%) together with recovery of 2-naphthol (518 mg, 72%).

(2) CCSC (**3**; 144 mg, 1.1 mmol) was added to a solution of 2-naphthol (144 mg, 1.0 mmol) and Bu_3N (204 mg, 1.1 mmol) in CH_2Cl_2 (2 mL) at 0-5 °C and the mixture was stirred at rt for 15 h. A silimar work up, described in (1), gave **6a** (58 mg, 18%) and **2a** (2 mg, 1%) together with recovery of 2-naphthol (67

mg, 47%). **6a**: Light yellow crystals; mp 212-216 °C; Anal. Calcd for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; S, 10.7. Found: C, 75.1; H. 4.6; S, 10.6. FDMS (Hitachi M-80B instrument; 3 kV) *m/z* 318 (M^+). These IR, ^1H and ^{13}C NMRs spectra accorded with those of the authentic sample.

Reaction of *p*-cresol with CCSC (3) / Bu3N in the absence of a Lewis acid catalyst: Following the similar procedure (2) described above, use of *p*-cresol (108 mg, 1.0 mmol) in the place of 2-naphthol gave bis(*p*-tolyl)sulfenate (**6b**; 77 mg, 31%) with only a trace amounts of 5-methyl-1,3-benzooxathiol-2-one (**2d**). **6b**: Light brown oil; Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.78. Found: C, 67.9; H. 5.4. IR (neat) ν_{max}: 3383, 1701, 1232 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.24 (6H, s), 6.89 (4H, d, J = 4.0 Hz), 7.03 (4H, d, J = 4.0 Hz); ^{13}C NMR ($CDCl_3$): δ = 29.1, 115.1, 129.6, 129.9, 153.5.

General procedure for preparing 1,3-benzooxathiol-2-ones (2): CCSC (**3**; 0.72g, 5.5 mmol) was added to a stirred mixture of phenol (5.0 mmol) and Bu3N (1.02 g, 5.5 mmol) in 1,2-dichloromethane (10 mL) at 0-5 °C and the mixture was stirred for 2 h at rt. After cooling to 0-5 °C, $AlCl_3$ (1.60 g, 12.0 mmol) was added portion by portion to the mixture, which was allowed to warm at rt and stirred for 10 h. Water was added to the mixture, which was extracted with CH_2Cl_2. The organic phase was washed with water and brine, dried (Na_2SO_4) and concentrated. The crude oil obtained was purified by silica gel column chromatography (hexane/EtOAc = 20:1-5:1) to give the corresponding 1,3-benzooxathiol-2-one (**2**).

Naphth[1,2-*d*]-1,3-oxathiol-2-one (2a).[17] Yellow crystals; mp 100-101 °C (*i*-PrOH) (lit., 107 °C); IR (KBr) ν_{max}: 1756, 1734, 1244, 808, 791, 766, 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 7.45-7.50 (1H, m), 7.51-7.58 (1H, m), 7.60-7.64 (2H, m), 7.85-7.91 (1H, m), 7.93-7.99 (1H, m); ^{13}C NMR ($CDCl_3$): δ = 111.7, 120.2, 123.6, 126.7, 127.2, 127.7, 127.9, 129.6, 130.7, 145.2, 169.0; MS (70eV) *m/z* (rel intensity) 202 (M^+, 57), 147 (14), 146 (100).

Naphth[2,1-*d*]-1,3-oxathiol-2-one (2b).[18] Light yellow crystals; mp 78-79 °C (*i*-PrOH) (lit., unlisted); IR (KBr) ν_{max}: 1752, 1730, 1211, 1015 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 7.25-7.55 (3H, m), 7.70-7.72 (1H, m), 7.85-7.87 (1H, m), 8.04-8.06 (1H, m); MS (70eV) *m/z* (rel intensity) 202 (M^+, 89), 174 (68), 146 (100).

1,3-Benzoxathiol-2-one (2c).[19] Yellow oil; IR (film) 1755 cm^{-1}; IR (KBr) ν_{max}: 1755, 1460, 1236, 1011 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.23-7.42 (4H, m); ^{13}C NMR ($CDCl_3$) δ = 112.01, 122.36,

123.04, 125.20, 127.49, 148.14, 168.68.

5-Methyl-1,3-benzoxathiol-2-one (2d).[18] Colorless crystals; mp 81.0-82.0 °C (Hexane-Benzene) (lit., unlisted); IR (KBr) ν_{max}: 1742, 1479, 1236, 1018 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.38 (3H, s), 7.10-7.20 (3H, m); ^{13}C NMR ($CDCl_3$) δ = 21.06, 111.56, 122.41, 122.78, 128.13, 135.21, 146.12, 168.98; MS (70eV) *m/z* (rel intensity) 166 (M^+, 88), 138 (17), 110 (100).

7-Methyl-1,3-benzoxathiol-2-one (2e). Colorless crystals; mp 62.0-64.0 °C; Anal. Calcd for $C_8H_6O_2S$: C, 57.81; H, 3.64. Found: C, 57.46; H. 3.57. IR (KBr) ν_{max}: 1742, 1460, 1236, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.40 (3H, s), 7.13-7.24 (3H, m); ^{13}C NMR ($CDCl_3$) δ = 15.18, 119.63, 122.55, 122.65, 124.89, 128.87, 146.81, 168.87.

5-Methyoxy-1,3-benzoxathiol-2-one (2f).[20] Colorless crystals; mp 75.0-76.0 °C (Hexane-Benzene) (lit., 73 °C); IR (KBr) ν_{max}: 1736, 1481, 1213, 1088 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.81 (3H, s), 6.83-7.20 (3H, m); ^{13}C NMR ($CDCl_3$) δ = 55.91, 107.33, 112.52, 113.50, 123.86, 142.19, 157.07, 168.91; MS (70 eV): *m/z* (rel intensity) 182 (M^+, 90), 154 (28), 126 (100).

5,7-Dimethyl-1,3-benzoxathiol-2-one (2g).[21] Colorless crystals; mp 64.9-65.5 °C (Hexane-Benzene) (lit., 66 °C); IR (KBr) ν_{max}: 1755, 1728, 1471, 1223 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.33 (3H, s), 2.35 (3H, s), 6.93 (1H, s), 7.01 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 15.74, 21.00, 119.70, 122.11, 122.32, 129.68, 134.81, 144.82, 169.19.

5-Chloro-7-methyl-1,3-benzoxathiol-2-one (2h). Yellow crystals; mp 94.0-95.5 °C (Hexane-Benzene); Anal. Calcd for $C_8H_5O_2ClS$: C, 47.89; H, 2.51. Found: C, 47.67; H. 2.47. IR (KBr) ν_{max}: 1763, 1456, 1192, 787 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.34 (3H, s), 7.13 (1H, s), 7.21 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 15.18, 119.39, 123.91, 124.08, 128.95, 130.13, 145.25, 168.01.

Typical procedure for preparing 4-methyl-2-sulfanylphenol (1d) by hydrolysis:

A mixture of 5-methyl-1,3-benzoxathiol-2-one (**2d**; 167 mg, 1.0 mmol) and 1 M-NaOH solution (H_2O:EtOH = 1:1; 2 mL) was stirred at 60 °C for 15 min under N_2 atmosphere. Water was added and the mixture was extracted with EtOAc, the organic phase was washed with water and brine, dried (Na_2SO_4) and concentrated. The crude oil obtained was purified by silica gel column chromatography (hexane/EtOAc=3:1) to give the product (**1d**)[24] (117 mg, 83%). Light yellow oil. IR (neat) ν_{max}: 3447, 1472, 1335 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.20 (3H, s), 3.30-3.40 (1H, br s), 5.89-6.22 (1H, br), 6.81-7.24 (3H, m).

1-Sulfanyl-2-naphthalenol (1a).[17] Yellow needles; mp 65.0-66.0 °C (Hexane) (lit., 65 °C); IR (KBr) ν_{max}: 3474, 1618, 1385 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 3.30-3.40 (1H, br s), 6.60 (1H, s), 7.01-7.04 (1H, m), 7.25-7.34 (2H, m), 7.71-7.79 (2H, m), 7.99-8.01 (1H, m).

2-Sulfanyl-1-naphthalenol (1b).[23] Light brown needles; mp 83.0-85.0 °C (Hexane) (lit., 81 °C); IR (KBr) ν_{max}: 3312, 1597, 1387cm^{-1}; ^1H NMR ($CDCl_3$): δ = 3.30-3.40 (1H, br s), 6.81-6.83 (1H, m), 7.62-7.50 (3H, m), 7.82-7.83 (1H, m), 8.17-8.19 (1H, m).

2-Methyl-6-sulfanylphenol (1e).[24] Light yellow oil; IR (neat) ν_{max}: 3450, 1584, 1460, 1424 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.26 (3H, s), 3.30-3.50 (1H, br s), 6.36 (1H, s), 6.71-6.73 (1H, m), 7.06-7.07 (1H, m), 7.19-7.20 (1H, m).

4-Methoxy-2-sulfanylphenol (1f).[25] Light yellow oil; IR (neat) ν_{max}: 3422, 1485, 1337 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 3.30-3.40 (1H, br s), 3.68 (3H, s), 5.82-5.92 (1H, br s), 6.71-6.73 (1H, m), 7.06-7.07 (1H, m), 7.19-7.20 (1H, m); MS (70 eV): *m/z* (rel intensity) = 156 (100), 141 (51), 113 (10), 85 (17).

2,4-Dimethyl-6-sulfanylphenol (1g).[26] Light yellow oil; IR (neat) ν_{max}: 3443, 1472, 1335 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.17 (3H, s), 2.32 (3H, s), 3.30-3.40 (1H, br s), 6.15-6.21 (1H, br), 6.82-6.85 (1H, m), 7.00-7.03 (1H, m); MS (70 eV): *m/z* (rel intensity) = 156 (100), 141 (51), 113 (10), 85 (17).

4-Chloro-6-methyl-2-sulfanylphenol (1h).[27] Yellow needles; mp 46.0-47.0 °C (Hexane, lit., 43-44 °C); IR (KBr) ν_{max}: 3420, 1460, 1323 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.24 (3H, s), 3.30-3.40 (1H, br s), 6.10-6.24 (1H, br s), 7.03-7.07 (1H, m), 7.19-7.29 (1H, m); MS (70 eV): *m/z* (rel intensity) = 176 (37), 174 (100), 141 (16), 139 (46).

Typical procedure for preparing 5-ethyl-4-methyl-1,3-oxathiol-2-one (7a).[11]

CCSC (**3**; 144 mg, 1.1 mmol) was added to a stirred solution of 3-pentanone (86 mg, 1.0 mmol) and Bu_3N (204 mg, 1.1 mmol) in EDC (2.0 mL) at rt. The mixture was heated at 80 °C for 3 h, and then cooled down. Water (5 mL) was added to the mixture, which was extracted with EtOAc. The organic phase was washed with water, brine, dried (Na_2SO_4), and concentrated to give a crude residue. This was purified by silica gel column chromatography (hexane/ethyl acetate = 20:1) to give **7a** (72 mg, 50 %). Red brown oil; IR (film) ν_{max}: 2963, 2938, 2367, 2344, 1759, 1653, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.17 (3H, t, *J* = 8 Hz), 2.04 (3H, s), 2.42 (2H, q, *J* = 8 Hz); ^{13}C NMR ($CDCl_3$) δ = 11.00, 11.97, 19.34, 108.42, 144.83, 193.18; MS (Int. %) 144 (M^+; 24), 116 (8), 85 (12), 59 (100).

Use of Et_3N (111 mg, 1.1 mmol) in the place of Bu_3N gave **7a** (16 mg, 6 %). The similar procedure, deccribed above, adding $AlCl_3$ (160 mg, 1.2 mmol) or $FeCl_3$ (178 mg, 1.1 mmol) before heating at 80 °C, **7a** (32 mg, 22 %) was obtained in either case.

4-Ethyl-5-propyl-1,3-oxathiol-2-one (7b).

Following the similar procedure for preparing **7a**, using 4-heptanone (114 mg, 1.0 mmol), **7b** (105 mg, 50%) was obtained. When the reaction was carried out at rt for 3 h, the yield is 61%. Yellow oil; IR (film) ν_{max}: 2967, 2936, 2367, 2343, 1753, 1460, 1125, 1033, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.93 (3H, t, J = 8 Hz), 1.00 (3H, t, J = 8 Hz), 1.59-2.02 (4H, m), 2.44-2.65 (2H, m); MS (70 eV) *m/z* (rel intensity) 172 (M^+; 34), 144 (5), 116 (6), 99 (9), 73 (100). Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02. Found: C, 55.5; H. 6.8.

5-Methyl-4-pentyl-1,3-oxathiol-2-one (7c).

Following the similar procedure for preparing **7a**, using 2-octanone (128 mg, 1.0 mmol), **7c** (86 mg, 46 %) was obtained. Red brown oil; IR (film) ν_{max}: 2959, 2932, 2363, 2342, 1761, 1458, 1026, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.87-0.93 (11H, m), 2.30 (3H, s); MS (70 eV) *m/z* (rel intensity) 186 (M^+; 33), 129 (10), 115 (100), 101 (11), 81 (46). Anal. Calcd for $C_9H_{14}O_2S$: C, 58.03; H, 7.58. Found: C, 57.9; H. 7.2.

Methyl 5-methyl-2-oxo-1,3-oxathiol-4-ylcarboxylate (7d).

Following the similar procedure for preparing **7a**, using methyl acetoacetate (116 mg, 1.0 mmol) at rt for 10 h, **7d** (94 mg, 54 %) was obtained as *s-cis* and *s-trans* mixtures. Red brown oil; IR (film) ν_{max}: 2959, 2370, 2350, 1759, 1726, 1439, 1292, 1107 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.50 (3Hx1/3, s), 2.53 (3Hx2/3, s), 3.85 (3Hx2/3, s), 3.93 (3Hx1/3, s); ^{13}C NMR ($CDCl_3$) δ = 13.95, 23.33, 52.62, 54.91, 155.14, 160.72, 168.31, 191.37, 195.44; MS (70 eV) *m/z* (rel intensity) 174 (M^+; 100), 146 (20), 143 (25), 100 (80), 88 (34), 87 (50), 69 (27). Anal. Calcd for $C_6H_6O_4S$: C, 41.38; H, 3.47. Found: C, 41.0; H. 3.2.

7-Methyl-4,5,6,7-tetrahydro-1,3-benzoxathiazol-2-one (7e).

Following the similar procedure for preparing **7a**, using 2-methylcyclohexanone (112 mg, 1.0 mmol) at rt for 5 h, **7e** (51 mg, 30 %) was obtained. Red brown oil; IR (film) ν_{max}: 2934, 2862, 2363, 2342, 1713, 1450, 1123 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.03 (3H, d, J = 7 Hz), 1.62-2.41 (7H, m); MS (70 eV) *m/z* (rel intensity) 170 (M^+; 6), 110 (42), 86 (22), 82 (61), 69 (78), 67 (100), 55 (89). Anal. Calcd for $C_8H_{10}O_2S$: C, 57.45; H, 5.92. Found: C, 57.0; H. 5.7.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture (Japan). One of the authors (Y. Y) acknowledges Sasakawa Scientific Research Grant from the Japan Science Society.

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Received, 11th June, 1998