Annulation of Ethyl [Bis(ethylthio)methyl]benzoate and Ethyl 2-[1,3]Dithiolan-2-yl-benzoate with α,β-Unsaturated Carbonyl Compounds: A New Synthesis of Naphthalene and Anthracene Derivatives

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Several kinds of fused cyclic compounds were obtained by tandem Michael-Claisen condensation of ethyl 2-[bis(ethylthio)methyl]benzoate and ethyl 2-[1,3]dithiolan-2-yl-benzoate with α,β-unsaturated carbonyl compounds. Treatment of the annulated products with mercury(II) perchlorate trihydrate or N-chlorosuccinimide gave naphthoquinones, naphthalenes, and anthracenes.

Key words [2C+4C] annulation; naphthalene; anthracene; tandem Michael-Claisen condensation; synthesis

Many naturally occurring and biologically active compounds contain phenolic rings. In previous papers, we have reported effective preparations of a variety of basic phenolic compounds, such as benzene-1,2-diols, benzene-1,3-diols and benzene-1,2,4-triols, via annulations of aliphatic compounds and we have employed them in total syntheses of natural products such as pterocarpons and aporphine alkaloids. This paper deals with a new procedure for synthesis of condensed aromatic compounds such as naphthalenes and anthracenes by [2C+4C] annulation.

Methyl bis(ethylthio)acetate (1) is useful in the preparation of benzene-1,2,4-triols (2). The anion of 1 is the initiator of the [2C+4C] annulation to give six-membered rings (3), which are converted to aromatic rings (2) by sequential hydrolysis and isomerization. Similar reactivity was expected with the vinylogous compound, ethyl 2-[bis(ethylthio)methyl]benzoate (4), which was prepared in good yield from 2-formylbenzoic acid (5a) via thiaacetatization and esterification.

Although the anion of 1 was generated easily by sodium hydride (NaH) in tetrahydrofuran (THF) at 0°C, that of 4 was not obtained in this way. It was formed by treatment of 4 with lithium disopropylamide in THF at −78°C. Reaction of the anion with methyl acrylate (6) in the presence of hexamethyolphosphoramide (HMPA) gave 4,4-bis(ethylthio)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (7) in 95% yield, through both Michael reaction at the β-carbon and Claisen reaction at the α carbon of 6. Several α,β-unsaturated carbonyl compounds such as methyl crotonate (8), butenolide (9), 2-cyclohexen-1-one (10), and 3-buten-2-one (11) were examined for reaction with 4. The yields of condensed products (7, 12—14) were good, as shown in Table 1. Although a similar annulated product, 2-acetyl-4,4-bis(ethylthio)-3,4-dihydro-2H-naphthalen-1-one (15a) was expected to be obtained via the condensation of 4 with 11, the reaction gave 2-acetyl-4-ethylthio-1-naphthalenol (15b) after purification. Inspection of the spectral data of the crude product showed the presence of compound 15a. This result indicated that compound 15a is labile under the ambient conditions, affording 15b by oxidative elimination. The cyclic keto esters 7 and 12 were also easily converted to the naphthalenes 25 and 29, respectively, on standing at room temperature. On the other hand, compounds 13 and 14 were stable, presumably because the existence of the third ring hinders the reaction of sulfur with atmospheric oxygen.

The thioacetate analog, ethyl 2-[1,3]dithiolan-2-yl-benzoate (16), could be obtained similarly from 5a. Condensation of the ester 16 with α,β-unsaturated carbonyl compounds (6, 8—11) was carried out to compare the reactivity of 4 and 16. The products (17—21) are shown in Table 1. The yields of the condensed products from compound 4 were higher than those from 16.

As compared with the cyclic thioacetal structure of compound 16, the two ethylthio groups in compound 4 have greater flexibility. The structural latitude of 4 is advantageous for the annulation reaction. Instability of the condensed products such as 7, 12, and 15a was attributed to the same flexibility of the substituents on the ring. In contrast, the fixed cyclic thioacetal compounds (17, 18, 21) corresponding to the bis(ethylthio)acetals (7, 12, 15a) were stable in contact with the atmosphere at...
Table 1. Tandem Michael-Claisen Reaction of the Benzoates 4 and 16

![Chemical structures and reactions](Chemical Structures)

In preceding investigations, we have established the conversion of six-membered rings with ethylthio groups to aromatic rings by sequential hydrolysis and isomerization. Similar transformation was applied to the annulated products (7, 12–14, 17–20) to obtain naphthalene and anthracene derivatives. N-Chlorosuccinimide (NCS)/acetone–H₂O and mercury(II) perchlorate trihydrate (MPC)/methanol–THF were used for hydrolysis of the thioacetales, as shown in Table 2.

Depending upon the combination of the thioacetales and the reagents, the reactions gave several kinds of aromatic compounds bearing two hydroxyl groups (22, 23), quinone carbonyl groups (24), a thio group (25–28), a chloro group (30–33), and a methoxyl group (34). Hydrolysis of 7 and 20 gave 22 and 23, respectively. The quinone 24 was the oxidative product of 2-methyl-1,4-naphthalediol generated from the thioacetales (12, 18). Compounds having a thio group (25, 26, 27, 28) were formed by incomplete hydrolysis of the acetals (7, 13, 14, 17, respectively). The chlorine atom on 30–32 was derived from NCS. The methoxyl group on 34 came from methyl alcohol used as the solvent. In methanolysis of the lactones (13, 19), an intermediate such as 4,4-dimethoxy-3,4,9a-tetrahydrodronaphtho[2,3-c]furan-1,9-dione might suffer elimination to give compound 34. The yields of aromatic compounds from the bis(thioethyl) derivatives (7, 12–14) with NCS or MPC were higher than those from the [1,3]dithiolan derivatives (17–20). The reactions of the open chain thioacetales (7, 12–14) and MPC gave especially good yields.

In conclusion, ethyl 2-[bis(ethylthio)methyl]benzoate (4) and ethyl 2-[1,3]dithiolan-2-yl-benzoate (16) were subjected to the tandem Michael-Claisen reaction. The reaction with several kinds of $\alpha,\beta$-unsaturated carbonyl compounds (6, 8–11) gave polyyclic compounds (7, 12–14, 15b, 17–21). Treatment of some of the condensed thioacetal derivatives with MPC or NCS gave naphthoquinone (24), naphthalenes (22, 25, 26, 28, 31–34), and anthracenes (23, 27, 30). The preparation of these aromatic compounds via annulation reactions demonstrates the utility of compounds 4 and 16 in syntheses of multifunctional condensed aromatic compounds.

### Experimental
IR spectra were recorded on a Hitachi 270-30 infrared spectrometer. 'H-NMR spectra were recorded with a JEOL JNM-PX600 600MHz spectrometer (600 MHz) or a JNM-GX270 FT spectrometer (270 MHz) using tetramethylsilane as an internal standard. Melting points were measured on a Yanaco MP model MP micro melting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX300 mass spectrometer. All organic extracts were dried over anhydrous MgSO₄. Column chromatography was performed with Kieselgel 60 (70–230 mesh).

**Ethyl 2-[bis(ethylthio)methyl]benzoate (4)** A mixture of compound 5b (16.5 g), anhydrous EtOH (200 mL), and H₂SO₄ (0.5 mL) was refluxed for 25 h. After evaporation of EtOH, water was added to the residue, and the product was extracted with AcOEt. The organic extract was washed with saturated aqueous NaHCO₃ and brine, and dried, then evaporated. The residue was subjected to column chromatography on silica gel with AcOEt–hexane (1: v/v) to give the title compound (4) as a colorless oil (15.0 g, 82%). IR (neat): 1720 cm⁻¹. ¹H-NMR 60 MHz, CDCl₃): $\delta$: 1.13–1.52 (9H, m, CO₂CH₂CH₃), SCH₂CH₃ x 2), 2.62 (4H, t, J = 7 Hz, SCH₂CH₃), 4.38 (2H, q, J = 7 Hz, CO₂CH₂CH₃), 6.28 (1H, s, CH(SCH₂CH₃)₂), 7.08–7.98 (4H, m, aromatic protons). Anal. Calcd for C₁₅H₁₂O₃S: C, 59.12; H, 7.09. Found: C, 59.37; H, 7.04.

**2-[bis(ethylthio)methyl]benzoic Acid (5b)** A mixture of 2-formylbenzoic acid (10.0 g) and p-toluenesulfonyl chloride (1.1 g) in ethanethiol (40 mL) was refluxed with stirring for 8 h. Excess ethanethiol was evaporated off under reduced pressure, then water was added to the residue and the product was extracted with AcOEt. The organic extract was washed with brine, dried, and evaporated in vacuo. The residue was crystallized from hexane to give 5b (15.9 g, 94%) as colorless needles, mp 98.0–99.0 °C. IR (Nujol): 1684 cm⁻¹. ¹H-NMR 60 MHz, CDCl₃): $\delta$ = 1.30 (6H, t, J = 7 Hz, CH(SCH₂CH₃)₂), 2.67 (4H, q, J = 7 Hz, CH(SCH₂CH₃)₂), 6.40 (1H, s, CH(SCH₂CH₃)₂), 7.15–8.13 (4H, m, aromatic protons). HRMS Calcd for C₁₅H₁₂O₂S: 256.0582 (M+). Found: m/z 256.0582 (M+)..

**2-[1,3]Dithiolan-2-yl-benzoic Acid (5c)** Titanium(IV) chloride (25.3 g) was added to a mixture of 2-formylbenzoic acid (20.0 g) and 1,2-ethanediol (18.9 g) in CH₂Cl₂ (200 mL) at 0 °C. The mixture was stirred at room temperature for 12 h, then poured into water. The organic layer was washed with water and brine, dried, and concentrated in vacuo. The residue was crystallized from benzene to give the title compound (5c) (98.3%, 94%) as colorless needles, mp 161–162 °C. IR (Nujol): 180 cm⁻¹. ¹H-NMR 60 MHz, CDCl₃): $\delta$: 3.40 (4H, brs, SCH₂CH₃), 6.75 (1H, s, SCH₂CH₃), 7.26–8.42 (4H, m, aromatic protons). HRMS Calcd for C₁₅H₁₃O₂S: 226.0122. Found: m/z 226.0125 (M+). Anal. Calcd for C₁₅H₁₃O₂S: C, 53.07; H, 4.45. Found: C, 53.09; H, 4.37.

**4,4-(bis-ethylthio)-1-oxo-1,2,3,4-tetrahydrodronaphthalene-2-carboxylic Acid Methyl Ester (7)** 4-Ethylthio-1-hydroxynaphthalene-2-carboxylic Acid Methyl Ester (25) A solution of diisopropylamine (3.5 mL) in dry THF (30 mL) was cooled to −78 °C in an atmosphere of Ar, and a
1.6 M solution of n-BuLi (23.3 mmol) in hexane was added dropwise. A solution of compound 4 (3.0 g, 10.6 mmol) and HMPA (1.8 ml) in dry THF (15 ml) was added to the reaction mixture over 10 min. Then a solution of methyl acrylate (2.3 ml) in dry THF (3 ml) was added dropwise at -90°C. Stirring was continued for 8 h at room temperature, and 10% HCl was added. The product was extracted with AcOEt, and the organic extract was washed with saturated aqueous NaHCO₃, water, and brine, and then dried. After evaporation in vacuo, the residue was crystallized from MeOH to give the title compound (7) as colorless needles (3.3 g, 95%), mp 61.5-63.0°C. IR (CHCl₃): 1656, 1624, 1596 cm⁻¹. ¹H-NMR (60 MHz, CDCl₃): δ: 1.13 (6H, t, J=7 Hz, SCH₂CH₂₂), 2.18-2.28 (4H, m, SCH₂CH₂₂ x 2), 3.15 (2H, brs, C(3H)₂), 3.83 (3H, s, COOC₃H₃), 7.16-8.00 (4H, m, aromatic protons). MS m/z: 262 (M⁺ - Set). Anal. Calc'd for C₁₅H₁₄O₂S₂: C, 59.23; H, 6.21. Found: C, 59.45; H, 6.33. Compound 7 was allowed to stand in contact with the atmosphere for 10 d at room temperature, and the product was crystallized from MeOH-H₂O to give 25 as pale yellow needles, mp 93-94°C (MeOH-H₂O). IR (CHCl₃): 1666, 1628, 1596 cm⁻¹. ¹H-NMR (60 MHz, CDCl₃): δ: 1.23 (3H, t, J=7 Hz, SCH₂CH₂₂), 2.85 (2H, q, J=7 Hz, SCH₂CH₂₂), 3.98 (3H, s, COOC₃H₃), 7.8-8.2 (2H, m, C(6H), C(7H), 8.00 (1H, s, C(3H)₂), 8.3-8.6 (2H, m, C(5H), C(8H)), HRMS Caled for C₁₅H₁₄O₂S₂: 262.0663. Found: m/z: 262.0662 (M⁺). Anal. Calc'd for C₁₅H₂₀O₃S₂: C, 64,10; H, 5.38. Found: C, 63.99; H, 5.40. 4,4-Bis(ethylthio)-3-methyl-1-oxo-1,2,3,4-tetrahydrobenzophenalen-2-carboxylic Acid Methyl Ester (12) and 4-Ethylthio-1-hydroxy-3-methylbenzophenalen-2-carboxylic Acid Methyl Ester (29) Compound 12 was prepared from 4 and methyl crotonate (8) in the same manner as described for 7 in 88% yield. Purification was performed by column chromatography [AcOEt-hexane (1:19, v/v)] to afford a pale yellow oil. IR (CHCl₃): 1650, 1622 cm⁻¹. ¹H-NMR (270 MHz, CDCl₃): δ: 0.94, 1.35 (each 3H, t, J=7.4 Hz, SCH₂CH₂₂ x 2), 1.07 (3H, d, J=6.9 Hz, C(3)-CH₃), 2.03 (1H, m, C(3H)₂), 3.10, 2.79 (each 2H, q, J=7.4 Hz, SCH₂CH₂₂ x 2), 3.85 (3H, s, OCH₃), 7.37, 7.42 (each 1H, dd, J=2, 7.5, 7.5 Hz, C(6H), C(7H)), 7.59, 7.90 (each 1H, dd, J=2, 7.5, 7.5 Hz, C(5H), C(8H)).
Spriol [1,3-dithiane-2,4,3'-3,4,9,4'-tetrahydropyrazolo[2,3-c][furan-1,9'-dione] (19) Compound 19 was prepared from 16 and butenolide (9) in the same manner as described for 7, in 68% yield. Purification was performed by column chromatography (AcOEt–hexane (1:1, v/v)) to afford colorless needles, mp 84–85 °C. IR (Nujol): 1652 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ 1.00 (3H, d, J = 7 Hz, C(3')-CH₃), 3.40 (4H, brs, SICH₂CH₂), 3.80 (3H, s, OCH₃), 7.2–8.0 (4H, m, aromatic protons). HRMS Caled for C₉H₁₀O₄: 210.0579. Found: m/z 210.0576 (M⁺).

Spriol [2-acetyl-bis(ethylthio)-3,4-dihydro-naphthalene-1,4'-2',[1,3]dithione] (20) Compound 20 was prepared from 16 and 2-cyclohexene-1-one (10) in the same manner as described for 7, in 62% yield. Purification was performed by column chromatography [AcOEt–hexane (1:1, v/v)] to afford colorless needles, mp 122–123 °C. IR (CHCl₃): 1594 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ 1.65–2.50 (7H, m), 3.46 (3H, s, C6H, C7H), 7.8–8.2 (4H, m, C6H, C7H, C8H). HRMS Caled for C₁₇H₁₄O₂S₄: 384.0951. Found: m/z 384.0958 (M⁺). Anal. Caled for C₁₇H₁₄O₂S₄: C, 53.96; H, 5.63. Found: C, 53.14; H, 5.63.

Reactions of Compound 7 with NCS: Formation of Compound 25 and 1,4-Dihydroxy-naphthalene-2-carboxylic Acid Methyl Ester (22) A solution of NCS (3 mmol) in H₂O acetonitrile (1:99, v/v) (5 mL) was added to a solution of 7 (1.5 mmol) in H₂O acetonitrile (5 mL: 1:99, v/v) at 20 °C. The mixture was stirred for 7 h at room temperature, then 5% aqueous Na₂SO₄ was added and the product was extracted with CH₂Cl₂. The organic extract was washed with water and brine, dried, and then evaporated in vacuo. The residue was subjected to column chromatography on silica gel with CH₂Cl₂ to give 25 in 85% and 5% yields, respectively. 22: Pale yellow needles, mp 180–183 °C (MeOH), (lit. (v) mp 192–193 °C). IR (CHCl₃), 1686 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ 3.95 (3H, s, OCH₃), 5.85 (2H, brs, OH×2), 7.10 (1H, s, C(3H)), 7.6–7.8 (2H, m, C(6H), C(7H)), 8.1–8.5 (2H, m, C(5H), C(8H)). MS m/z: 218 (M⁺).

Reactions of Compound 7 with MPC: Formation of Compound 25 A solution of mercury(I)perchlorate trihydrate (0.71 mmol) in MeOH–THF (3:1, v/v) (5 mL) was added to a solution of 7 (3.6 mmol) in MeOH–THF (3:1, v/v) (10 mL) at room temperature. Stirring was continued for 6 h, then saturated aqueous NaNO₂ and CH₃CO₂H (20 mL) were added to the reaction mixture, and the whole was filtered. The filtrate was separated and the organic layer was washed with water and brine, dried, and then evaporated. The residue was subjected to column chromatography on silica gel with CH₂Cl₂ to give the title compound (25) in 97% yield.

Reactions of Compound 12 with NCS: Formation of 3-Methyl-1,4-dioxo-1,4-dihydroxy-naphthalene-2-carboxylic Acid Methyl Ester (24) Compound 12 was treated with NCS to give 24 in 73% yield in the same manner as described for 7. Purification was performed by column chromatography [AcOEt–hexane (1:1, v/v)] to afford colorless needles, mp 75–77 °C (MeOH), (lit. (v) mp 70 °C). IR (CHCl₃): 1740, 1668 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ 2.15 (3H, s, C(3H)), 3.92 (3H, s, OCH₃), 7.41–7.92 (2H, m, C(6H), C(7H)), 8.2–8.2 (2H, m, C(5H), C(8H)). HRMS Caled for C₁₇H₁₄O₅: 320.0579. Found: m/z 320.0576 (M⁺).

Spirool [3,1-dithiolo-2,4'-1'-oxo-1',2',3',4'-tetrahydropyrazolo[2,3'-furan-1,9'-dione] (18) Compound 18 was prepared from 16 and methyl crotonate (8) in the same manner as described for 7, in 72% yield. Purification was performed by column chromatography [AcOEt–hexane (1:1, v/v)] to afford colorless needles, mp 94–95 °C (MeOH). IR (CHCl₃): 1650, 1622 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ 1.00 (3H, d, J = 7 Hz, C(3')-CH₃), 3.40 (4H, brs, SICH₂CH₂), 3.80 (3H, s, OCH₃), 7.2–8.0 (4H, m, aromatic protons). HRMS Caled for C₉H₁₀O₄: 210.0579. Found: m/z 210.0576 (M⁺).

Reactions of Compound 13 with NCS: Formation of 4-Ethylthio-3-hydroxy-3-naphthalene-2-carboxylic Acid Methyl Ester (18) Compound 13 was prepared from 16 and methyl crotonate (8) in the same manner as described for 7, in 65% yield. Purification was performed by column chromatography [AcOEt–hexane (1:1, v/v)] to afford colorless needles, mp 140–155 °C (MeOH). IR (Nujol): 3388, 1756, 1640, 1595 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ 1.17 (3H, J = 7 Hz, SICH₂CH₂), 2.73 (3H, J = 7 Hz, SICH₂CH₃), 2.54 (3H, s, C(3H)), 7.5–7.7 (2H, m, C(6H), C(7H)). 8.2–8.6 (2H, m, C(5H), C(8H)).
C(8H)]. Anal. Caled for C₁₄H₁₉O₂S: C, 64.60; H, 4.65. Found: C, 64.30; H, 4.56.

Compound 18 was treated with MPCI to give 24 in 67% yield in the same manner as described for 7. Purification was performed by column chromatography [AcOEt-hexane (1:9, v/v)].

Reaction of Compound 19 with NCS: Formation of 4-Chloro-9-hydroxy-3H-naphtho[2,3-c]thuran-1-one (32) Compound 19 was treated with NCS to give 31 in 72% yield in the same manner as described for 7. Purification was performed by column chromatography (CH₂Cl₂).

Pale yellow needles, mp 238°C (MeOH). IR (Nujol): 3412, 1748, 1648 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ: 5.44 (2H, s, -CH₂O), 7.6–7.9 [2H, m, C(6)H, C(7)H], 8.2–8.5 [2H, m, C(5)H, C(8)H]. HRMS Caled for C₁₄H₁₁ClO₂: 234.0086. Found: m/z 234.0087 (M⁺).

Reaction of Compound 19 with MPCI: Formation of Compounds 34 Compound 19 was treated with MPCI to give 34 in 81% yield in the same manner as described for 7. Purification was performed by column chromatography [AcOEt-hexane (1:4, v/v)].

Reaction of Compound 13 with MPCI: Formation of 9-Hydroxy-4-methoxy-3H-naphtho[2,3-c]thuran-1-one (34) Compound 13 was treated with MPCI to give 34 in 81% yield in the same manner as described for 7. Purification was performed by column chromatography [AcOEt-hexane (1:4, v/v)].

Compound 34 was isolated as a pale yellow oil. IR (CHCl₃): 3488, 1736 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ: 5.97 (3H, s, OCH₃), 5.52 (2H, s, CH₂O), 7.5–7.8 [2H, m, C(6)H, C(7)H], 8.0–8.4 [2H, m, C(5)H, C(8)H]. Anal. Caled for C₁₄H₁₁O₂: 230.0579. Found: m/z 230.0579 (M⁺).

Reaction of Compound 14 with NCS: Formation of 10-ethylthio-9-hydroxy-3,4-dihydro-2H-anthracene-1-one (27) and 10-Chloro-9-hydroxy-3,4-dihydro-2H-anthracene-1-one (30) Compound 14 was treated with NCS to give 27 and 30 in 39% and 38% yields, respectively, in the same manner as described for 7. Purification was performed by column chromatography [AcOEt-hexane (1:9, v/v)].

Pale yellow needles, mp 116–118°C (MeOH). IR (Nujol): 1634, 1580 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ: 1.16 (3H, J = 7 Hz, SCH₂CH₃), 2.20 [2H, m, C(3)H₂], 2.70 [4H, m, C(4)H₄, SCH₂CH₃], 3.10 [2H, br, C(2)H₂], 7.1–7.6 [2H, m, C(6)H, C(7)H], 7.9–8.2 [2H, m, C(5)H, C(8)H]. Anal. Caled for C₁₄H₁₄O₂S: C, 70.56; H, 5.92. Found: C, 70.34; H, 5.98.


Reaction of Compound 16 with MPCI: Formation of Compound 27 Compound 16 was treated with MPCI to give 27 in 82% yield in the same manner as described for 7. Purification was performed by column chromatography [AcOEt-hexane (1:9, v/v)].

Reaction of Compound 17 with NCS: Formation of 3-Chloro-4-hydroxy-naphthalen-2-carboxylic acid methyl ester (33) Compound 17 was treated with NCS to give 33 in 46% yield in the same manner as described for 7. Purification was performed by column chromatography [AcOEt-hexane (1:9, v/v)].

Pale yellow needles, mp 121°C. IR (CHCl₃): 1672 cm⁻¹. 1H-NMR (60 MHz, CDCl₃): δ: 4.01 (3H, s, CH₃), 7.5–7.8 [2H, m, C(6)H, C(7)H], 7.88 [1H, s, C(3)H], 8.2–8.5 [2H, m, C(5)H, C(8)H]. HRMS Caled for C₁₃H₁₀ClO₂: 236.0239. Found: m/z 236.0211 (M⁺).

Reaction of Compound 17 with MPCI: Formation of Bis[4-hydroxy-3-methoxy-carbonyl-1-naphthyl]thiophenylthiato]mercury (28) Compound 17 was treated with MPCI to give 28 in 90% yield in the same manner as described for 7. Purification was performed by column chromatography [AcOEt-hexane (1:4, v/v)]. Pale yellow needles, mp 178–179°C (Acetone). IR (CHCl₃): 1670 cm⁻¹. 1H-NMR (270 MHz, CDCl₃): δ: 3.10 (4H, m, SCH₂CH₃), 3.92 (3H, s, CH₃O), 7.60 [2H, m, C(6)H and C(7)H], 7.91 [1H, s, C(3)H], 8.30 [2H, m, C(5)H and C(8)H]. MS m/z: 586 (M⁺ – C₃H₆O₂) Anal. Caled for C₂₆H₂₄N₂O₄S: C, 42.71; H, 3.33. Found: C, 42.64; H, 3.36.

References and Notes
1. A part of this study was presented at the 111th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, March 1991, and the 112th Annual Meeting of the Pharmaceutical Society of Japan, Fukuoka, March 1992.


