Ring-expansion of Some Sulfur-containing Heterocyclic Compounds with Dimethyl Acetylenedicarboxylate

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A number of *S*-heterocyclic 7-, 8- and 9-membered ring compounds belonging to the benzo[*b*]thiepin, benzo[*b*]thiocin, and benzo[*b*]thionin systems have been prepared through [2+2]cycloaddition of dimethyl acetylenedicarboxylate to enamines, *β*-keto-ester anions and one *β*-diketone anion. In the addition to the 5-membered ring compound, 3-hydroxy-2-methoxycarbonylbenzo[*b*]thiophene, a fluorescent by-product has been identified as an α-pyrone besides the main product, a benzo[*b*]thiepin.

In a research program concerning medium-size ring compounds containing sulfur, we have studied the [2+2]-cycloaddition of nucleophilic compounds to dimethyl acetylenedicarboxylate (DMAD), followed by electrocyclic ring opening. This paper describes the access to the benzo[*b*]thiepin, the benzo[*b*]thiocin, and the benzo[*b*]thionin systems *via* such reactions. Compounds belonging to these systems have a seven-, and eight-, or a nine-membered ring containing one sulfur atom and are thus representatives of rather unusual structure types.

Cycloaddition to enamines. Dutch workers have described the cycloaddition of DMAD to 3-(1-pyrrolidino)benzo[*b*]thiophene, followed by ring opening.[1] This leads to a benzo[*b*]thiepin. The next larger ring system is obtained in a similar addition to the pyrrolidine enamine of thiochroman-3-one.[2] A plan to perform the analogous reaction sequence starting with the readily available[3] thiochroman-4-one initially met with difficulty, since the corresponding enamine could not be prepared through azeotropic water removal.[4] The method using a

stoichiometric amount of titanium tetrachloride as condensation agent[5] was successful, however. The pyrrolidine enamine reacts with DMAD in tetrahydrofuran solution, and the cyclobutene adduct is stable, at room temperature for at least two weeks. It can be obtained as a viscous liquid in a purity sufficient for spectral characterization through chromatography on neutral alumina. On the contrary, chromatography on silica gel causes hydrolysis to a *β*-keto ester.

The initial adduct can be thermally rearranged to an eight-membered ring compound by heating at 150 °C for 1 h. The latter compound easily crystallizes. Since silica gel caused formation of the corresponding eight-membered ring *β*-keto ester, we suspected the cyclobutene–butadiene interconversion to be acid-catalyzed. However, treatment of the initial adduct in tetrahydrofuran solution either with acetic acid or trifluoroacetic acid, with or without water present, gave none of the eight-membered ring compounds; heating alone appears to be the best method. The catalytic action of silica gel is evidently due to other factors than its acidity.

The syntheses are illustrated in Scheme 1. The *β*-keto ester is drawn as its enol form, which is supported by ¹H NMR.

The analogous expansion from a seven- to a nine-membered ring has also been carried out. From the easily available[6] 5-oxo-2,3,4,5-tetrahydrobenzo[*b*]thiepin, the pyrrolidine enamine was prepared.[5] Addition of DMAD in tetrahydrofuran solution gave an 84 % yield of the nine-membered ring compound, 2,3-dihydro-5,6-bis-methoxycarbonyl-7-(1-pyrrolidinyl)benzo[*b*]thionin. In this case, the electrocyclic ring opening is fast enough at

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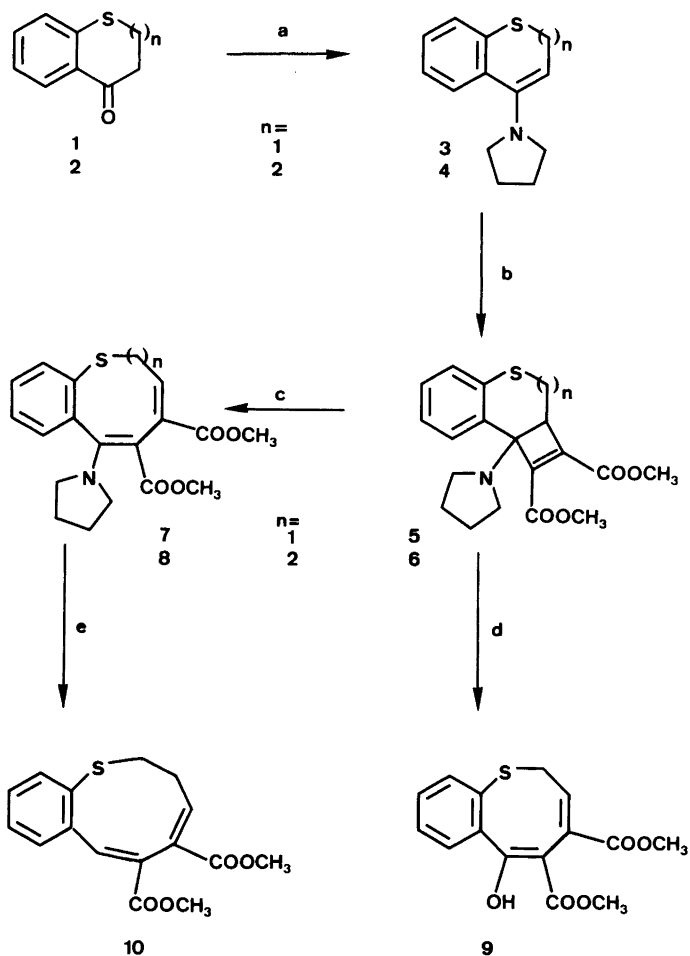
Scheme 1. Cycloaddition to enamines. Conditions: *a* pyrrolidine, TiCl$_4$, *b* dimethyl acetylenedicarboxylate, *c* n=1; 150 °C, 1 h, n=2; room temp., *d* silica gel chromatography; *e* B$_2$H$_6$.

or below room temperature to prevent the observation of the initial cyclobutene adduct.

Upon treatment with diborane, cyclic enamine esters undergo reductive C−N bond cleavage to yield unsaturated esters.[7] This reaction, when applied to the above enamine ester, gave the expected 2,3-dihydro-5,6-bis-methoxycarbonyl-benzo[*b*]thionin in 72 % yield. See Scheme 1.

Cycloaddition to β-ketoester anions. DMAD undergoes cycloaddition to the conjugate bases of carbocyclic β-keto esters[8] and their *N*-heterocyclic analogues.[9] We have now extended this reaction to a five- and a six-membered ring S-heterocyclic β-keto ester, respectively, and the expected seven- and

eight-membered rings have been obtained.

In the reaction of the five-membered ring compound, 3-hydroxy-2-methoxycarbonylbenzo[*b*]-thiophene, a by-product was formed in *ca.* 1 % yield. It was detected because of its fluorescence, which also aided in the separation from the main product, 5-hydroxy-2,3,4-tris-methoxycarbonyl-benzo[*b*]thiepin. High-resolution MS gave for the by-product the molecular formula C$_{15}$H$_{10}$O$_6$S. The ^{1}H NMR spectrum shows four aromatic H atoms and two CH$_3$O groups. Of two reasonable isomeric structures accounting for these data, one is denoted *15* and is shown in Scheme 2. Its rational name is 3,4-bis-methoxycarbonyl-2-oxo-2*H*[1]-
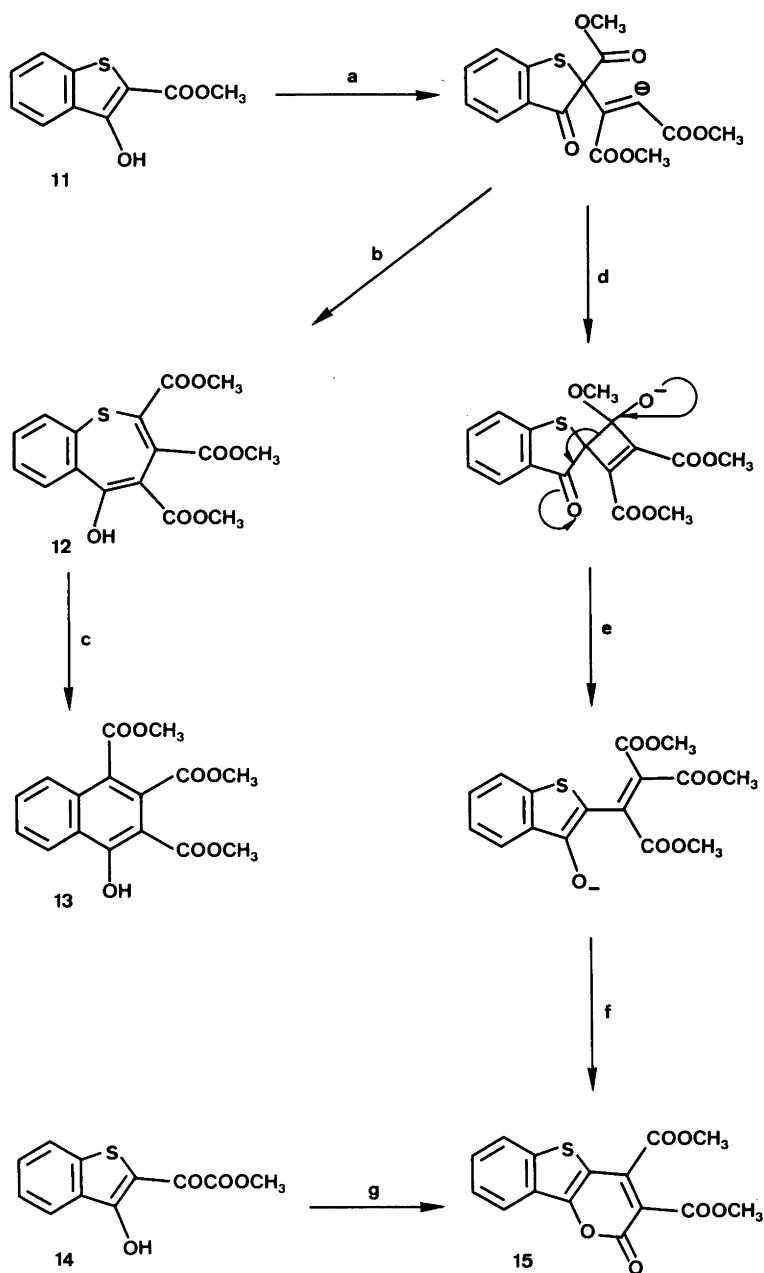
Scheme 2. Reactions of 3-hydroxy-2-methoxycarbonylbenzo[*b*]thiophene. Conditions: *a, b* NaH, then dimethyl acetylenedicarboxylate followed by acid work-up, *c* 180 °C, 1 h, *a,d,e,f* possible route to lactone, *g* ClCOCH$_2$COOCH$_3$, triethylamine.

benzothieno[3,2-b]pyran. An analogous lactone has been obtained as one of the products from addition of DMAD to 1,2-dihydro-2-ethoxycarbonyl-1-methylindol-3-one.[9] A mechanism involving a spirocyclic intermediate has been suggested,[9] for the formation of the lactone, and the same mechanism may be applied to our case; see Scheme 2.

It is also possible to envisage a route leading to 2,3-bis-methoxycarbonyl-4-oxo-4H-[1]benzothieno[3,2-b]pyran. However, this isomer is an α,β-unsaturated ketone (a γ-pyrone) and would not be expected to be fluorescent, as was pointed out by Dr. H.-D. Becker. In fact, a compound containing a 2,3-dicarboxyl-substituted γ-pyrone ring annealed to a benzene ring, 2-ethoxycarbonyl-4-oxochromen-3-carboxylic acid, is known,[10] and no mention of fluorescence is made. An independent synthesis of 15 from a glyoxylic ester was carried out (Scheme 2), and the properties of the material thus obtained were identical with those of the by-product. Structure 15 is therefore ascertained.

The benzo[b]thiepin compound is colourless and stable at room temperature. Like known analogues,[1,11] it suffers extrusion of sulfur upon heating, yielding 2,3,4-tris-methoxycarbonyl-1-naphthol.

The cycloaddition of DMAD to the anion of 3-methoxycarbonylthiochroman-4-one is illustrated in Scheme 3 together with the synthesis of the keto ester. The latter was obtained via decarbonylation after condensation of thiochroman-4-one with dimethyl oxalate.[12] The attempted preparation of 3-methoxycarbonylthiochroman-4-one according to a different literature procedure[13] failed completely. The latter route involves Dieckmann cyclization of methyl 2-(2-cyanoethyl)thiobenzoate, but we found that this compound upon treatment with base as described[13] instead undergoes retro-cyanoethylation. Methyl 2-mercaptobenzoate was the only aromatic compound obtained. The conclusions in Ref. 13 were based on IR, but not NMR, spectra and must be regarded with the utmost suspicion.

Cycloaddition to a β-diketone anion. Like β-keto esters, β-diketones might be expected to add DMAD via their conjugate bases. As one representative example, 3-acetylthiochroman-4-one was chosen. This diketone was easily prepared through acylation of an enamine. According to ^{1}H NMR, it is completely enolic and is more adequately named 3-acetyl-4-hydroxy-2H-thiochromene. Its conjugate base, generated with sodium hydride, reacts with DMAD to form, after ring opening, 3-acetyl-6-hydroxy-4,5-bis-methoxycarbonyl-2H-benzo[b]-thiocin. The synthesis is illustrated in Scheme 4.

EXPERIMENTAL

General comments. Most syntheses were performed at least twice, and the yields were reproducible. Reactions involving air- or moisture-sensitive compounds were routinely performed under nitrogen using magnetic stirring. The term "usual work-up" means distribution of the reaction mixture
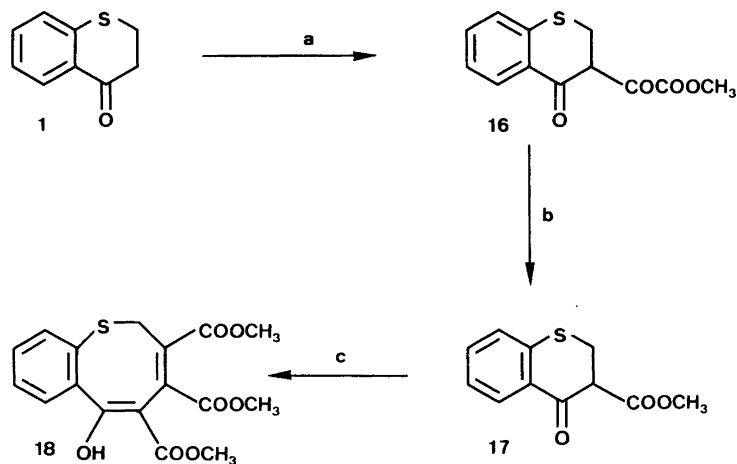
Scheme 3. Synthesis of 6-hydroxy-3,4,5-tris-methoxycarbonyl-2H-benzo[b]thiocin. Conditions: a dimethyl oxalate, CH₃ONa, b 180 °C, 30 min, c dimethyl acetylenedicarboxylate.
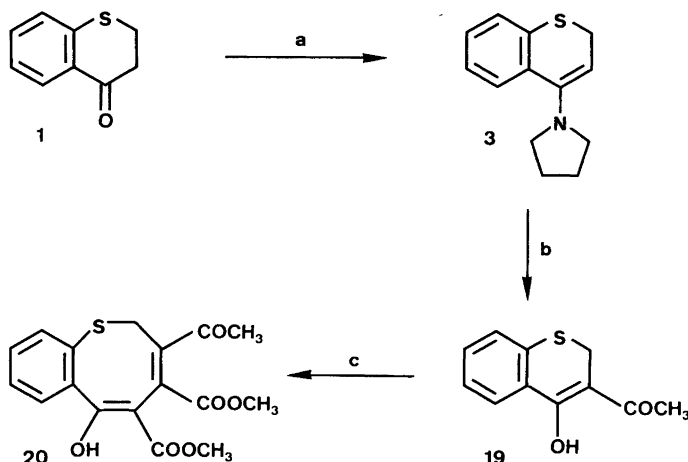
Scheme 4. Synthesis of 3-acetyl-6-hydroxy-4,5-bis-methoxycarbonyl-2*H*-benzo[*b*]thiocin. Conditions: *a* pyrrolidine, TiCl$_4$, *b* acetyl bromide, *c* NaH, then dimethyl acetylenedicarboxylate followed by acid work-up.

between water and an appropriate solvent, in most cases, dichloromethane, washing the organic phase with water followed by brine, drying over magnesium sulfate or sodium sulfate and removal of the solvent at aspirator pressure. Solids were recrystallized from solvents specified under each compound. A technique often successful in removing coloured impurities is filtration through a short silica gel column. Solvents used in ester condensation, enamine formation and cycloaddition reactions were dried before use.

Abbreviations: Dimethyl acetylenedicarboxylate DMAD, tetrahydrofuran, THF.

Instruments for spectrometry: Bruker WH 270 FT NMR, and AEI MS 902 mass spectrometer. Melting points have been determined with a Kofler Hot Stage microscope. Elemental analyses were carried out by Novo Microanalytical Laboratory, Bagsvaerd, Denmark.

Thiochroman-4-one (1) and 5-oxo-2,3,4,5-tetrahydrobenzo[b]*thiepin (2)* were prepared according to literature procedures.[3,6]

4-(1-Pyrrolidinyl)-2H-thiochromene (3). To a solution of 16.4 g (0.1 mol) of *1* and 42.5 g (0.6 mol) of pyrrolidine in 50 ml of benzene and 50 ml of hexane, 10 g (52 mmol) of titanium tetrachloride was added dropwise at −10 °C. The resulting light brown suspension was stirred for 24 h at room temperature, filtered, and evaporated. The residue, a semi-crystalline mass, was used directly in the following steps. Yield 17.4 g (80 %), ¹H NMR (270 MHz, CDCl$_3$): δ 1.80−1.92 (4 H, m), 2.86−2.96 (4 H, m), 3.27 (2 H, d, *J* 6 Hz), 5.17 (1 H, t, *J* 6 Hz), 7.07−7.48 (4 H, m).

2,3-Dihydro-5-(1-pyrrolidinyl)benzo[b]*thiepin (4).* A mixture of 60 g (0.34 mol) of *2*, 78.5 g (1.1 mol) of pyrrolidine, 100 ml of benzene, and 100 ml of hexane was cooled to −10 °C. At this temperature, 32.5 g (0.17 mol) of titanium tetrachloride was added dropwise. After 48 h, the reaction mixture was filtered and the liquid part evaporated at reduced pressure. The residue, a yellowish-red oil, was pure enough for the following steps. Yield 63 g (81 %), ¹H NMR (270 MHz, CDCl$_3$): δ 1.82−1.87 (4 H, m), 1.99−2.05 (2 H, m), 2.90−2.95 (4 H, m), 3.24−3.29 (2 H, m), 4.97 (1 H, t, *J* 8 Hz), 7.17−7.57 (4 H, m).

7,8-Bis-methoxycarbonyl-6-(1-pyrrolidinyl)-3-thia-4,5-benzobicyclo[4.2.0]*octa-4,7-diene (5).* To a solution of 21.7 g (0.1 mol) of *3* in 70 ml of THF was added during 1 h a solution of 14.2 g (0.1 mol) of THF was added during 1 h a solution of 14.2 g (0.1 mol) of DMAD in 20 ml of THF. The addition took place at 0 °C, and the mixture was left for 48 h at room temperature. After evaporation of the solvent at reduced pressure, the resulting dark oil was chromatographed on neutral alumina with dichloromethane as the eluent. The main fraction was evaporated to give a reddish oil which was essentially pure according to NMR. Keeping at room temperature for two weeks provoked no change. The yield was 22.3 g (62 %). ¹H NMR (270 MHz, CDCl$_3$); δ 1.78−1.83 (4 H, m), 2.53−2.62 (2 H, m), 2.73 (1 H, dd, *J* 13 and 3 Hz), 2.72−2.80 (2.80 (2 H, m), 3.21 (1 H, dd, *J* 13 and 3 Hz), 3.63 (3 H, s), 3.73 (3 H, t, *J* 3 Hz), 3.81 (3 H, s), 7.06−7.24 (3 H, m), 8.11−8.16 (1 H, m).

4,5-Bis-methoxycarbonyl-6-(1-pyrrolidinyl)-2H-benzo [b]*thiocin (7).* The purified oil *5*, 22.3 g, was

kept at 150 °C for 1 h and allowed to cool. Crystals were obtained through trituration with ether. They were separated and dissolved in dichloromethane. Filtration through a short silica gel column removed some impurities, and upon evaporation of the eluate, colourless crystals, 18 g (50 % from 3), were obtained, m.p. 143 – 145 °C. ^{1}H NMR (270 MHz, CDCl$_3$): δ 1.77 – 2.00 (4 H, m), 2.93 – 3.03 (2 H, m), 3.20 – 3.40 (2 H, m), 3.39 (1 H, dd, J 10 and 7 Hz), 3.61 (3 H, s), 3.62 (3 H, s), 3.88 (1 H, t, J 10 Hz), 6.26 (1 H, dd, J 10 and 7 Hz), 7.09 – 7.27 (4 H, m). Anal. C$_{19}$H$_{21}$NO$_4$S: C, H, S.

2,3-Dihydro-5,6-bis-methoxycarbonyl-7-(1-pyrrol-idinyl)-benzo[b]*thionin (8).* To a solution of 21 g (90 mmol) of 4 in 175 ml of THF was added a solution of 21 g (90 mmol) of 4 in 175 ml of THF was added a solution of 14.2 g (0.1 mol) of DMAD in 15 ml of THF at 0 °C during 1 h. After 36 h, the solution was evaporated to give a greenish, crystalline residue. After the same purification as for 7, colourless crystals were obtained, 28.4 g (84 %), m.p. 170 – 172 °C, ^{1}H NMR (270 MHz, CDCl$_3$): δ 1.81 – 1.95 (4 H, m), 2.49 – 2.63 (2 H, m), 2.93 – 3.23 (4 H, m), 3.39 (3 H, s), 3.37 – 3.51 (2 H, m), 3.64 (3 H, s), 6.78 (1 H, dd, J 11.5 and 4 Hz), 7.08 – 7.12 (1 H, m), 7.21 – 7.25 (2 H, m), 7.51 – 7.55 (1 H, m). Anal. C$_{20}$H$_{23}$NO$_4$S: C, H, S.

6-Hydroxy-4,5-bis-methoxycarbonyl-2H-benzo-[b]*thiocin (9).* To a solution of 21.7 g (0.1 mol) of 3 in 70 ml of toluene was added a solution of 14.2 g (0.1 mol) of DMAD in 30 ml of toluene at 0 °C during 3 h. After 48 h at room temperature, 25 ml of acetic acid was added, and the reaction mixture was left overnight. The solvent was removed at reduced pressure and the residue was dissolved in a mixture of dichloromethane, acetic acid and water. Enough silica gel was added to produce a thick slurry, which was left for 48 h. After filtration and evaporation, the residue was chromatographed (silica gel – dichloromethane) to give 11.3 g (40 %) of colourless crystals, m.p. 100 – 101 °C, ^{1}H NMR (270 MHz, CDCl$_3$): δ 2.78 (1 H, dd, J 17.2 and 6.9 Hz), 3.19 (1 H, dd, J 17.2 and 6.9 Hz), 3.66 (3 H, s), 3.70 (3 H, s), 4.34 (1 H, t, J 6.9 Hz), 7.52 – 7.61 (3 H, m), 7.89 (1 H, s), 8.52 – 8.56 (1 H, m). Anal. C$_{15}$H$_{14}$O$_5$S: C, H, S.

2,3-Dihydro-5,6-bis-methoxycarbonylbenzo[b]*-thionin (10).* A solution of 11.2 g (30 mmol) of 8 in 100 ml of THF was cooled to 0 °C. Gaseous diborane (100 mmol), generated *ex situ*,[14] was introduced. After 20 h, the reaction mixture was evaporated to dryness. Ethyl acetate, 50 ml, was added. The solution was filtered, evaporated and chromatographed on silica gel, first with dichloromethane, later with dichloromethane – methyl acetate 9:1 as the eluent. After evaporation of the main fraction and trituration with ether, 6.8 g (72%) of colourless crystals were obtained, m.p. 132 – 134 °C. ^{1}H NMR (270

MHz, CDCl$_3$): δ 2.62 – 3.01 (4 H, m), 3.64 (3 H, s), 3.84 (3 H, s), 6.75 (1 H, t, J 8 Hz), 6.91 – 6.97 (1 H, m), 7.20 – 7.26 (2 H, m), 7.55 – 7.59 (1 H, m), 8.13 (1 H, s). Anal. C$_{16}$H$_{16}$O$_4$S: C, H, S.

3-Hydroxy-2-methoxycarbonylbenzo[b]*thiophene (11)* was prepared according to the literature.[15]

5-Hydroxy-2,3,4-tris-methoxycarbonylbenzo[b]*-thiepin (12).* Sodium hydride dispersion, 2.1 g (45 mmol NaH), was washed with hexane and suspended in 50 ml of toluene, and 8 g (40 mmol) of 11 was added. After the hydrogen evolution had ceased, 5.7 g (40 mmol) of DMAD in 20 ml of toluene was added during 1 h at 0 °C. After 3 days at room temperature, acetic acid was carefully added until the suspension had dissolved. Usual work-up gave a partially crystallized mass. The crystals, consisting of starting material, 1.4 g, were removed and the remainder chromatographed on silica gel with toluene as the eluent. The main fraction was contaminated with a strongly fluorescent (yellowish-green) compound, which could be removed through its very low solubility in methanol. The main product was obtained as colourless crystals, 3.7 g (41 %), m.p. 123 – 125 °C. ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.68 (3 H, s), 3.80 (3 H, s), 3.82 (3 H, s), 7.42 – 7.46 (3 H, m), 7.80 – 7.84 (1 H, m), 13.69 (1 H, s). Anal. C$_{16}$H$_{14}$O$_7$S: C, H, S.

2,3,4-Tris-methoxycarbonyl-1-naphthol (13). In a sealed glass ampoule, 0.3 g of 12 was heated at 180 °C for 1 h. A yellowish, crystalline mass was formed upon cooling. Recrystallization gave a quantitative yield of colourless crystals, m.p. 94 – 96 °C. ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.90 (3 H, s), 3.95 (3 H, s), 3.96 (3 H, s), 7.59 – 7.75 (2 H, m), 8.13 – 8.18 (1 H, m), 8.45 – 8.50 (1 H, m), 12.40 (1 H, s). MS [IP 34 eV; m/e (% rel. int.)]: 318 (38.8), 287 (31), 286 (100), 241 (8.3), 228 (25), 227 (10.8), 198 (19.2), 171 (11.1), 170 (70.4). Mol. wt., obs. 318.0723, calc. for C$_{16}$H$_{14}$O$_7$ 318.0740.

3-Hydroxy-2-methoxalylbenzo[b]*thiophene (14).* To a solution of 7.5 g (50 mmol) of 3-hydroxy-benzo[b]thiophene[16] and 8.3 g (70 mmol) of dimethyl oxalate in 100 ml of methanol was added a solution of 50 mmol of sodium methoxide (from 1.15 g of sodium) in 100 ml of methanol. The mixture turned dark red within seconds. After a 10 min reflux period, a solution of 5 ml of conc. hydrochloric acid in 50 ml of methanol was added to the cold reaction mixture. A brick-red precipitate formed, which was filtered off and recrystallized from 250 ml of methanol – acetone 5:1. The hot solution was filtered to remove a dark-coloured, amorphous impurity. Orange, slender needles were obtained, m.p. 137 – 138 °C, 4.15 g (35 %). ^{1}H NMR (270 MHz, CDCl$_3$): δ 4.02 (3 H, s), 7.38 – 8.04 (4 H, m), 12.67 (1 H, s). Anal. C$_{11}$H$_8$O$_4$S: C, H, S.

3,4-Bis-methoxycarbonyl-2-oxo-2H-[1]benzo-thieno[3,2-b]*-pyran (15).* By-product in the synthesis

of 12: The fluorescent material virtually insoluble in methanol amounted to 100 mg, m.p. 226 – 227 °C. Attempted ^{13}C NMR failed because of insufficient solubility in a number of solvents including DMSO-d_6. ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.98 (3 H, s), 4.04 (3 H, s), 7.46 – 7.61 (2 H, m), 7.83 – 7.86 (1 H, m), 8.06 – 8.09 (1 H, m). MS [IP 50 eV; m/e (% rel. int.)]: 318 (100), 290 (28.3), 287 (22.6), 259 (14.3), 173 (23), 144 (13.6), 104 (16). Mol. wt., obs. 318.0167, calc. for C$_{15}$H$_{10}$O$_6$S 318.0198.

Independent synthesis of 15 from 14: A solution of 4 g (17 mmol) of *14* and 2 g (20 mmol) of triethylamine in the minimum amount of benzene was treated with small portions of methyl chloroformyl acetate (prepared from the potassium salt of malonic acid monomethyl ester and thionyl chloride^{17}) until a 20 % excess had been added. Crystals were immediately formed in the reaction mixture. The solvent was removed at reduced pressure and the triethylamine hydrochloride was washed away with water. The remainder, yellow crystals, amounted to 3 g (56 %). The ^{1}H NMR spectrum was identical with that of the by-product described above. M.p. and mixed m.p. 226 – 227 °C.

3-Methoxalylthiochroman-4-one (16) and *3-methoxycarbonylthiochroman-4-one (17)* were prepared according to the literature.^{12}

6-Hydroxy-3,4,5-tris-methoxycarbonyl-2H-benzo-[b]thiocin (18). Sodium hydride dispersion, 1.7 g (35 mmol NaH), was washed with hexane and suspended in 50 ml of toluene. To this mixture was added 6.44 g (29 mmol) of *17* in 25 ml of toluene. After the hydrogen evolution had ceased, 4.12 g (29 mmol) of DMAD in 15 ml of toluene was added at 0 °C during 1 h. After 24 h at room temperature, acetic acid, 10 ml, was carefully added, followed by 60 ml of 2 M hydrochloric acid and 100 ml of toluene. After usual work-up, the crude product was recrystallized from methanol to yield 7.81 g (74 %) of colourless crystals, m.p. 146 – 150 °C with decomposition. ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.55 (1 H, d, J 11.2 Hz), 3.63 (3 H, s), 3.71 (3 H, s), 3.79 (3 H, s), 4.20 (1 H, d, J 11.2 Hz), 7.25 – 7.30 (4 H, m), 12.94 (1 H, s). Anal. C$_{17}$H$_{16}$O$_7$S: C, H, S.

3-Acetyl-4-hydroxy-2H-thiochromene (19). To a solution of 34.7 g (0.16 mol) of *3* and 16.2 g (0.16 mol) of triethylamine in 100 ml of chloroform, a solution of 19.7 g (0.16 mol) of acetyl bromide in 50 ml of chloroform was added during 30 min. The mixture was refluxed for 2 h. Water, 60 ml, and conc. hydrochloric acid, 60 ml, were added, and refluxing was continued for another 2 h. The cooled organic phase was washed with water and extracted 3 times with 1 M potassium hydroxide. The alkaline solution was acidified with hydrochloric acid and extracted with chloroform. After drying, filtration and evaporation of the solvent, the remainder was recrystallized from methanol to yield 13.2 g (40 %)

of yellow needles, m.p. 82 – 84 °C. ^{1}H NMR (270 MHz, CDCl$_3$): δ 2.26 (3 H, s), 3.72 (2 H, s), 7.18 – 7.28 (3 H, m), 7.94 – 7.97 (1 H, m), 16.52 (1 H, s). Anal. C$_{11}$H$_{10}$O$_2$S: C, H, S.

3-Acetyl-6-hydroxy-4,5-bis-methoxycarbonyl-2H-benzo[b]thiocin (20). Sodium hydride dispersion, 3.1 g (60 mmol NaH), was washed with hexane and suspended in 80 ml of toluene. Of *19*, 10.3 g (50 mmol) was added in portions. When the hydrogen evolution had ceased, 7.1 g (50 mmol) of DMAD was added at 0 °C during 2 h. After 24 h at room temperature, 20 ml of acetic acid was carefully added, followed by 100 ml of 2 M hydrochloric acid and 200 ml of toluene. After the usual work-up, recrystallization from methanol gave 13.2 g (76 %) of colourless crystals, m.p. 124 – 128 °C. ^{1}H NMR (270 MHz, CDCl$_3$): δ 2.07 (3 H, s), 3.36 (1 H, d, J 11 Hz), 3.64 (3 H, s), 3.78 (3 H, s), 4.21 (1 H, d, J 11 Hz), 7.31 – 7.35 (4 H, m), 12.87 (1 H, s). Anal. C$_{17}$H$_{16}$O$_6$S: C, H, S.

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