Preparation of 2-Bromopropionyl Bromide-d_4. Ethyl bromide-d_5 (10.0 g) (Merck and Co., Inc., 99 atom % D) was converted to ethylmagnesium bromide-d_5 with 2.7 g of magnesium in 60 ml of ether. Carbonation by addition to excess carbon dioxide gave 4.64 g (68%) of propionic acid-d_5. Conversion to 2-bromopropionic acid-d_4 was accomplished by treatment with 10.0 g of bromine and 0.5 ml of phosphorus trichloride at 80–95 °C for 6 h. The crude bromo acid was treated with 15.9 g of phosphorus tribromide and the mixture was refluxed for 30 min. The crude product was distilled through a Vigreux column. After a small forerun of propionyl bromide, 16.2 g of a mixture of 2-bromopropionyl bromide-d_4 and an unknown impurity was obtained, bp 55–61 °C (16 mm).

Preparation of Bromo Ketones 10 and 11. The procedure was essentially that of Brady and Roe.[18] The 2-bromopropionyl bromide mixture obtained above in 30 ml of hexane was added over a 1.5-h period to a solution of 9.5 g of triethylamine in 65 ml of cyclopentadiene and 70 ml of hexane at room temperature. After filtration and an aqueous workup, the crude residue was distilled through a Vigreux column. The first fraction, bp 69.5–73 °C (1.3 mm), 1.69 g, was about 77% exo bromo ketone **10.** The second fraction, bp 73–80 °C (1.3 mm), 2.83 g, was about 70% endo bromo ketone **11.**

Preparation of *endo*-6-Methyl-d_3-*exo*-bicyclo[3.1.0]hex-2-enecarboxylic Acid (12). A 1.69-g sample of the bromo ketone mixture enriched in exo bromo ketone **10** was vigorously stirred for 2 h at room temperature with a solution of 1.13 g of lithium hydroxide in 11.5 ml of water. The solution was extracted with ether and the aqueous phase was added to a cold hydrochloric acid solution. The precipitate was collected and air dried giving 0.879 g (75%) of acid **12,** mp 65–70 °C. Conversion of **12** to triflate **9b** was completely analogous to the preparation of **9a.**[16]

Kinetic Procedure. The procedure was followed as previously described.[2a] For runs at 25 °C, the time was recorded when the end points of the titrations were reached. The rate constants reported represent the average of a minimum of two determinations.

Registry No.—5, 56552-97-7; **10,** 60153-89-1; **11,** 60208-18-6; **12,** 60184-59-0; trifluoromethanesulfonic anhydride, 358-23-6; 1-methyl-d_3-cyclopropanol, 60153-90-4; 2-bromopropionyl bromide-d_4, 60153-91-5; ethyl bromide-d_5, 3675-63-6; propionic acid-d_5, 60153-92-6; 2-bromopropionic acid-d_4, 60153-93-7; cyclopropyl methyl ketone, 765-43-5; 7-acetylbicyclo[4.1.0]heptene, 10330-36-6; *exo*-6-acetylbicyclo[3.1.0]hexane, 10330-37-7; *endo*-6-acetylbicyclo[3.1.0]-hexane, 60153-94-8.

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Thianaphthen-2-one Chemistry. 2. The Benzylidene Thiolactone Rearrangement: Synthesis of 2-Arylthianaphthene-3-carboxylic Acids and Esters

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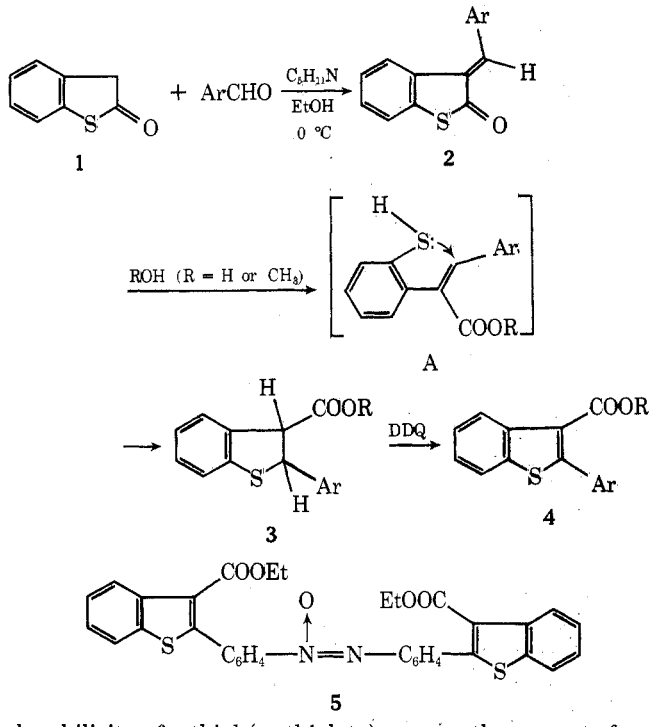
The condensation of thianaphthen-2-one and aromatic aldehydes gave the corresponding 3-benzylidenethianaphthen-2-ones (**2**). Treatment of the benzylidene derivatives with ethanolic potassium hydroxide followed by acidification gave 2-aryl-2,3-dihydrothianaphthene-3-carboxylic acids (**3a–c**), while refluxing the benzylidene derivatives with methanol gave the methyl 2-aryl-2,3-dihydrothianaphthene-3-carboxylates (**3d, 3e**) (benzylidene thiolactone rearrangement). Oxidation of the dihydro acids and esters with DDQ (2,3-dichloro-5,6-dicyano-1,4-quinone) gave the corresponding 2-arylthianaphthene-3-carboxylic acids and esters (**4a–d**).

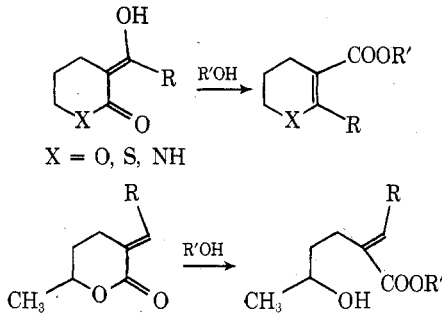
Earlier studies in these laboratories on the condensation of thianaphthen-2-one (**1**) with salicylaldehydes[1,2] led us to investigate the condensation of simple aryl aldehydes with **1** as a route to 3-benzylidenethianaphthen-2-ones (**2**). In the only prior report on such derivatives, Marschalk synthesized (Scheme I) 3-(2-methoxybenzylidene)thianaphthen-3-one (**2a**) which he claimed underwent hydrolytic scission to the mercaptostilbenecarboxylic acid (A) (Ar = o-$CH_3OC_6H_4$).[3] Having previously established the facile internal Michael addition of thiols to similarly activated double bonds,[1,2] we have reinvestigated Marschalk's claim and have found that the actual product is 2-(2-methoxyphenyl)-2,3-dihydrothianaphthene-3-carboxylic acid (**3a**).[4] This transformation of **2** to **3** resembles the well-known α-acyllactone rearrangement. However, there is no precedent for an α-benzylidenelactone undergoing this rearrangement, and other related α-exocyclic unsaturated lactones apparently experience only ring cleavage to hydroxy acid derivatives[5] (Scheme II). The enhanced nu-

Scheme I



Scheme II

Acyllactone rearrangement



cleophilicity of a thiol (or thiolate) apparently accounts for this special reaction of benzylidene thiolactones.

We wish to report a general procedure for the preparation of 3-benzylidenethianaphthen-2-ones (**2**), their unique rearrangement to 2-aryl-2,3-dihydrothianaphthene-3-carboxylic acids and esters (**3**) (benzylidene thiolactone rearrangement), and the subsequent oxidation of these dihydro derivatives to 2-arylthianaphthene-3-carboxylic acids and esters (**4**).

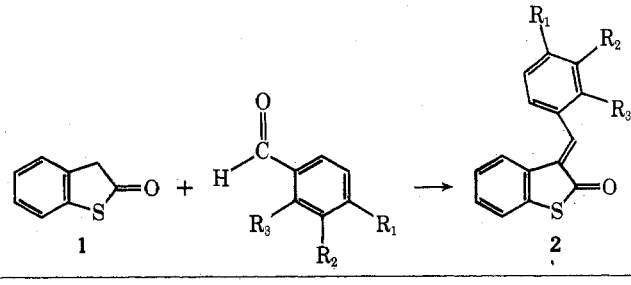
Benzylidene Derivatives (2a–g). 3-Benzylidenethianaphthen-2-ones were readily prepared by condensation, at ice bath temperatures, of **1** and an aryl aldehyde in ethanol containing a catalytic amount of piperidine. Reactions effected by heating did not yield pure products and sometimes led to mixtures of the rearranged 2-aryl-2,3-dihydrothianaphthene-3-carboxylates and other anomalous products.

The benzylidenes obtained (Table I) were yellow to red in color and displayed characteristic carbonyl absorptions at 1685 ± 5 cm^{-1}. In the NMR, the vinylic protons appear within the aromatic complex and the downfield position of these vinyl resonances implies the more thermodynamically favored trans configuration (vinyl proton cis to carbonyl). Previous reports in closely related systems indicated a greater anisotropic deshielding for trans vinyls than for similar cis isomers.[6,7,8]

Benzylidene Thiolactone Rearrangement. Conversion of 3-Benzylidenethianaphthen-2-ones to 2-Aryl-2,3-dihydrothianaphthene-3-carboxylic Acids and Esters (3a–e). The hydrolytic ring opening of 3-benzylidenethianaphthen-2-ones with alcoholic potassium hydroxide followed by acidification provided a convenient high-yield synthesis of the previously unknown 2-aryl-2,3-dihydrothianaphthene-3-carboxylic acids (**3a–c**). These dihydro acids (Table II) were readily identified by their NMR spectra, the methinyl protons appearing as downfield doublets with $J = 6$–9 Hz.[9] 2-(4-Nitrophenyl)-2,3-dihydrothianaphthene-3-carboxylic acid could not be obtained by the benzylidene thiolactone rearrangement. The reaction of 3-(4-nitrobenzylidene)thianaphthen-2-one (**2g**) with ethanolic potassium hydroxide gave a large amount of carbonaceous material from which was isolated, in low yield (33%), a compound identified as **5**. The azoxy compound apparently arises from the ethanolysis of the thiolactone to the dihydro ester which undergoes concomitant oxidation–reduction. In retrospect, the formation of the azoxy compound seems reasonable since alcohols readily open thiolactones (vide infra) and nitrobenzene is readily converted to azoxybenzene by refluxing in ethanolic potassium hydroxide.[10,11]

The benzylidene thiolactone rearrangement was further extended to the preparation of the previously unknown methyl 2-aryl-2,3-dihydrothianaphthene-3-carboxylates (**3d, 3e**) by refluxing the corresponding 3-benzylidene thiolactones in methanol with a catalytic amount of piperidine. The dihydro esters (Table II) were also easily identified by their

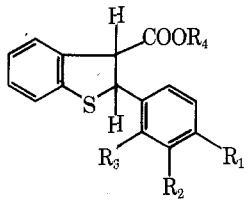
Table I.[a] 3-Benzylidenethianaphthen-2-ones



Registry no.	Compd	R_1	R_2	R_3	% yield	Mp, °C
55757-17-0	**2a**	H	H	OCH_3	65	96.5–98.5 (lit. 96–98)[b]
55757-19-2	**2b**	$-OCH_2O-$		H	54	162.0–162.5
60224-05-7	**2c**	OCH_3	H	OCH_3	83	146.5–148.0
60224-06-8	**2d**	$N(CH_3)_2$	H	H	75	160.0–163.0 (lit. 164–165)[b]
60224-07-9	**2e**	OH	H	OCH_3	84	173.0–175.0
60224-08-0	**2f**	Cl	H	H	86	137.0–138.0
60224-09-1	**2g**	NO_2	H	H	80	155.0–157.0

[a] Satisfactory analytical data [±0.3% for C, H, S (N)] were obtained on all new compounds listed. [b] C. Marschalk, *J. Prakt. Chem.*, **88**, 227 (1913).

Table II.[a] 2-Aryl-2,3-dihydrothianaphthene-3-carboxylates

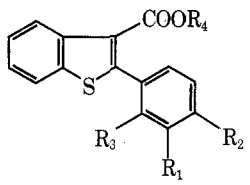


3

Registry no.	Compd	R_1	R_2	R_3	R_4	% yield	Mp, °C
55757-18-1	3a	H	H	OCH_3	H	84	139.0–140.0 (lit. 134–136)[b]
55757-21-6	3b	$-OCH_2O-$		H	H	78	186.0–187.5
60224-10-4	3c	OCH_3	H	OCH_3	H	77	163.0–164.0
60224-11-5	3d	$N(CH_3)_2$	H	H	CH_3	85	111.5–112.5
60224-12-6	3e	$-OCH_2O-$		H	CH_3	60	104.0–105.0

[a] Satisfactory analytical data [±0.3% for C, H, S (N)] were obtained on all new compounds listed. [b] C. Marschalk, *J. Prakt. Chem.*, **88**, 227 (1913).

Table III.[a] 2-Arylthianaphthene-3-carboxylates



4

Registry no.	Compd	R_1	R_2	R_3	R_4	% yield	Mp, °C
60224-13-7	4a	H	H	OCH_3	H	66	227.5–229.0
60224-14-8	4b	OCH_3	H	OCH_3	H	46	226.0–227.0
60224-15-9	4c	$N(CH_3)_2$	H	H	CH_3	55	130.5–131.5
60224-16-0	4d	$-OCH_2O-$		H	CH_3	82	85.0–86.0
6774-41-0	4e	H	H	H	H	33[b]	185.5–189.0 (lit. 188–189)[c]

[a] Satisfactory analytical data [±0.3% for C, H, S (N)] were obtained on all new compounds listed. [b] Prepared directly without isolation or purification of intermediate; see text for experimental method. [c] A. Chow et al., *J. Med. Chem.*, 9, 551 (1966).

NMR spectra which showed the methinyl protons, as in the case of the dihydro acids, as characteristic downfield doublets.

2-Arylthianaphthene-3-carboxylic Acids and Esters (4a–e). The 2-aryl-2,3-dihydrothianaphthene-3-carboxylic acids and esters obtained from the benzylidene thiolactone rearrangement were oxidized with DDQ in benzene to the corresponding 2-arylthianaphthene-3-carboxylic acids and esters (**4a–d**). The fully oxidized products (Table III) were characterized by the disappearance of the methinyl protons in the NMR and a shift of carbonyl frequencies in the infrared. The combined rearrangement and oxidation sequence represents a new and general two-step synthesis of these acids and esters. Previous syntheses of these compounds have involved multistep reactions.[12,13]

Finally, as further evidence for the structure of the rearrangement products, a literature compound, 2-phenylthianaphthene-3-carboxylic acid (**4e**), was prepared.[13] This involved the direct condensation and rearrngement of 1 and benzaldehyde to methyl 2-phenyl-2,3-dihydrothianaphthene-3-carboxylate. The crude ester was oxidized and subsequently hydrolyzed to 2-phenylthianaphthene-3-carboxylic acid.

Experimental Section

Infrared spectra were recorded on a Beckman IR 33 spectrophotometer as Nujol mulls or in solution using 0.1-mm sodium chloride liquid cells. NMR spectra were obtained on a Hitachi Perkin-Elmer R-20A spectrometer with tetramethylsilane as the internal standard.

Microanalyses were performed by Dr. G. I. Robertson, Jr., Florham Park, N.J. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

Procedure for the Preparation of 3-Benzylidenethianaphthen-2-ones (2a–g). A solution or slurry of 1.00 g (6.6 mmol) of thianaphthen-2-one[14,15] and the aromatic aldehyde (6.6 mmol) in 5 ml of absolute ethanol was cooled in an ice bath. Piperidine (3–7 drops) was added and stirring with ice bath cooling was continued for 3–8 h. The reaction mixture was then refrigerated overnight. Filtration and washing with cold 95% EtOH gave the crude product. Recrystallization from 95% EtOH gave the analytically pure benzylidene with the exception that **2e** was recrystallized from CH_3CN.

Procedure for the Preparation of 2-Aryl-2,3-dihydrothianaphthene-3-carboxylic Acids (3a–c). A solution or slurry of 3–4 mmol of the requisite benzylidene (**2a–c**) in 60 ml of absolute ethanol was treated with 10 ml of ethanolic KOH (0.7 g/10 ml). Any undissolved solid was soon solubilized and the initially intense orange to red color of the solution lightened. The solvent was removed in vacuo and the crude white potassium salt of the product was dissolved in a minimum of cold distilled water (10–25 ml) and acidified by dropwise addition of concentrated HCl to an oil which solidified on scratching.

2-(2-Methoxyphenyl)-2,3-dihydrothianaphthene-3-carboxylic Acid (3a). Recrystallization of the crude material, prepared as above, from benzene–petroleum ether (60–110 °C) gave 84% of white solid, mp 138.0–139.0 °C (lit. 134–136 °C).[3] An additional recrystallization gave 57%: mp 139.0–140.0 °C; NMR ($CDCl_3$) δ 3.82 (s, 3 H, OCH_3), 4.50 (d, 1 H, J = 6 Hz, CHCO), 5.75 (d, 1 H, J = 6 Hz, CHS), 6.62–7.80 (m, 8 H, ArH), 11.02 (s, 1 H, OH); ir ($CHCl_3$) 3400–2400 (br), 1700 cm^{-1}.

2-(3,4-Methylenedioxyphenyl)-2,3-dihydrothianaphthene-3-carboxylic Acid (3b). The crude product was recrystallized from benzene–petroleum ether (60–110 °C) to yield 78% of a white, fluffy solid, mp 185.5–187.0 °C. Recrystallization from benzene–petroleum ether gave a fluffy, white analytical sample: mp 186.0–187.5 °C; NMR (acetone-d_6) δ 4.48 (d, 1 H, J = 9 Hz, CHCO), 5.40 (d, 1 H, J = 9 Hz,

CHS), 5.95 (s, 2 H. OCH_2O), 6.58–7.48 (m, 7 H, ArH), 8.20–9.10 (broad, 1 H, OH, exchangeable with D_2O); ir (Nujol) 3400–2400 (br), 1695 cm^{-1}.

2-(2,4-Dimethoxyphenyl)-2,3-dihydrothianaphthene-3-carboxylic Acid (3c). Recrystallization from ethanol–water gave 77% of fine, yellow crystals: mp 163.0–164.0 °C; NMR (Me_2SO-d_6) δ 3.73 and 3.82 (two singlets of equal intensity, 6 H, OCH_3), 4.55 (d, 1 H, J = 6 Hz, CHCO), 5.57 (d, 1 H, J = 6 Hz, CHS), 6.30–6.70 (m, 2 H, ArH), 6.90–7.70 [m, 6 H, ArH, one proton (COOH) exchangeable with D_2O]; ir ($CHCl_3$) 3400–2400 (br), 1700 cm^{-1}.

Preparation of Methyl 2-Aryl-2,3-dihydrothianaphthene-3-carboxylates. Methyl 2-(4-Dimethylaminophenyl)-2,3-dihydrothianaphthene-3-carboxylate (3d). A slurry of 1.00 g (6.6 mmol) of **1** and 0.99 g (6.6 mmol) of *p*-dimethylaminobenzaldehyde in 5 ml of absolute ethanol was cooled in an ice bath prior to the addition of 10 drops of piperidine. A deep red solution resulted after approximately 20 min and at the end of 3 h blood red crystals of the benzylidene (**2d**) had separated. The reaction mixture was evaporated and the benzylidene was suspended in 30 ml of MeOH containing 2 ml of piperidine. After 20 h of reflux, an orange solution had formed which upon evaporation gave a light orange solid. Recrystallization from MeOH yielded 1.75 g (85%) of white crystals (**3d**): mp 109–110 °C; NMR ($CDCl_3$) δ 2.87 [s, 6 H, $N(CH_3)_2$], 3.68 (s, 3 H, OCH_3), 4.48 (d, 1 H, J = 9 Hz, CHCO), 5.42 (d, 1 H, J = 9 Hz, CHS), 6.43–7.52 (m, 8 H, ArH); ir ($CHCl_3$) 1730 cm^{-1}. An analytical sample of **3d** was prepared by recrystallization from MeOH: 1.40 g (68%) of stout, white needles, mp 111.5–112.5 °C.

Methyl 2-(3,4-Methylenedioxyphenyl)-2,3-dihydrothianaphthene-3-carboxylate (3e). Five drops of piperidine was added to a chilled solution of 1.00 g (6.6 mmol) of **1** and 1.00 g (6.6 mmol) of piperonal in 5 ml of absolute ethanol. A gummy orange solid was evident at the end of 2.5 h of stirring. Rotary evaporation gave the crude benzylidene (**2b**) which was dissolved in 20 ml of MeOH containing 1 ml of piperidine. After 5 h of reflux, rotary evaporation gave a yellow solid which was recrystallized from MeOH and air dried to 1.25 g (60%) of white crystals (**3e**): mp 102.0–103.0 °C; NMR ($CDCl_3$) δ 3.73 (s, 3 H, OCH_3), 4.38 (d, 1 H, J = 9 Hz, CHCO), 5.37 (d, 1 H, J = 9 Hz, CHS), 5.87 (s, 2 H, OCH_2O), 6.53–7.50 (m, 7 H, ArH); ir ($CHCl_3$) 1730 cm^{-1}. Recrystallization from methanol gave the analytical sample, mp 104.0–105.0 °C.

Procedure for the Preparation of 2-Arylthianaphthene-3-carboxylic Acids (4a, 4b). A solution of equimolar amounts (2.0–2.5 mmol) of the dihydro acid, either **3a** or **3c**, and DDQ in 20 ml of benzene was refluxed with stirring for 22 h. The hydroquinone was removed by hot filtration and the filtrate evaporated to approximately 10 ml. Chilling gave the dehydrogenated product which was recrystallized once from benzene to analytical purity, see Table III. **4a**, ir (Nujol) 3200–2400, 1665 cm^{-1}; **4b**, ir (Nujol) 3200–2400, 1670 cm^{-1}.

Procedure for Preparation of Methyl 2-Arylthianaphthene-3-carboxylate (4c, 4d). Equimolar amounts (3.5 mmol) of DDQ and either **3d** or **3e** were refluxed with stirring in 15 ml of anhydrous benzene for 18 h. The hydroquinone which had precipitated was filtered from the hot solution and rotary evaporation yielded a gummy oil. Trituration and subsequent recrystallization from MeOH gave the title compounds.

Methyl 2-(4-Dimethylaminophenyl)thianaphthene-3-carboxylate (4c). Recrystallization from methanol gave 55% of yellow solid (**4c**): mp 130.5–131.5 °C; NMR ($CDCl_3$) δ 2.90 (s, 6 H, NCH_3), 3.78 (s, 3 H, OCH_3), 6.50–8.40 (m, 8 H, ArH); ir ($CHCl_3$) 1705 cm^{-1}.

Methyl 2-(3,4-Methylenedioxyphenyl)thianaphthene-3-carboxylate (4d). Recrystallization from methanol gave 82% of fluffy cream-colored solid (**4d**), mp 84.0–85.0 °C. A second recrystallization from methanol yielded 63% of cream solid: mp 85.0–86.0 °C; NMR ($CDCl_3$) δ 3.82 (s, 3 H, OCH_3), 5.98 (s, 2 H, OCH_2O), 6.90–8.50 (m, 7 H, ArH); ir ($CHCl_3$) 1710 cm^{-1}.

Preparation of 2-Phenylthianaphthene-3-carboxylic Acid (4e). A solution of 1.00 g (6.6 mmol) of thianaphthen-2-one and 0.70 g (6.6 mmol) of benzaldehyde with 1 ml of triethylamine in 10 ml of methanol was refluxed for 6 h. Evaporation in vacuo gave the crude methyl dihydro ester as a brown oil: NMR ($CDCl_3$) δ 3.62 (s, 3 H, OCH_3), 4.43 (d, 1 H, J = 8 Hz), 5.42 (d, 1 H, J = 8 Hz), methinyl characteristic of the 2,3-dihydro system; ir (neat) 1735 cm^{-1}. The crude dihydro ester was then refluxed with 1.47 g (6.5 mmol) of DDQ in 20 ml of benzene for 14 h. The brown hydroquinone was removed by hot filtration through a sintered glass funnel and the filtrate was rotary evaporated to give the crude methyl 2-phenylthianaphthene-3-carboxylate as a red oil: NMR ($CDCl_3$) δ 3.68 (s, OCH_3), methinyls lacking; ir (neat) 1710 cm^{-1}. The crude ester was then saponified by refluxing with a potassium hydroxide solution (2.0 g KOH/125 ml) for 2.5 h. Acidification, filtration, and recrystallization from 50/50 ethanol–water gave 0.55 g (33% overall yield) of off-white acid: mp 185.5–189.0 °C (lit. 188–189 °C);[13] ir (Nujol) 3200–2400, 1660 cm^{-1}.

Preparation of 4,4′-Bis(3-carboethoxy-2-benzothienyl)-azoxybenzene (5). Ten milliliters of a hot ethanolic potassium hydroxide solution (0.7 g/10 ml ethanol) was added to a yellow-orange slurry of 1.00 g (3.5 mmol) of 3-(4-nitrobenzylidene)thianaphthen-2-one (**2g**) forming a dark black solution. The color slowly faded and a solid precipitated. The reaction mixture was evaporatgd to a black solid and this was slurried with 25 ml of distilled water. Acidification with concentrated HCl and filtration gave a dark green-black solid. Recrystallization of this material from benzene–petroleum ether (60–110 °C) produced 0.50 g of dark black carbonaceous solid, mp ≃300 °C, NMR (Me_2SO-d_6) only broad aromatic region. Evaporation of the filtrate from the recrystallization and digestion of the residue with hot acetone gave 0.35 g (33%) of the golden azoxy compound (**5**): mp 192.0–194.0 °C; NMR ($CDCl_3$) δ 1.18 (t, 3 H, J = 7 Hz, OCH_2CH_3), 4.27 (q, 2 H, J = 7 Hz, OCH_2CH_3), 7.20–8.60 (m, 8 H, ArH); ir ($CHCl_3$) 1700 cm^{-1}. Recrystallization from acetonitrile–chloroform gave golden-colored crystals of the analytical sample, mp 193.0–194.0 °C.

Anal. Calcd from $C_{34}H_{26}N_2O_5S_2$: C, 67.31; H, 4.32; N, 4.62; S, 10.57. Found: C, 67.56; H, 4.50; N, 4.79; S, 10.36.

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Registry No.—**1**, 496-31-1; **4e** methyl dihydro ester, 60224-17-1; **5**, 60224-18-2; benzaldehyde, 100-52-7; benzaldehyde (R_1R_2 = H; R_3 = OCH_3), 123-11-5; benzaldehyde (R_1R_2 = $-OCH_2O-$; R_3 = H), 120-57-0; benzaldehyde (R_1R_3 = OCH_3; R_2 = H), 613-45-6; benzaldehyde (R_2R_3 = H; R_1 = $N(CH_3)_2$), 100-10-7; benzaldehyde (R_1 = OH; R_2 = H; R_3 = OCH_3), 18278-34-7; benzaldehyde (R_2R_3 = H; R_1 = Cl), 104-88-1; benzaldehyde (R_2R_3 = H; R_1 = NO_2), 555-16-8.

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