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The Synthesis and Properties of *p*-,*p*′-Disubstituted Phenyl Thiolbenzoates:

A Class of Nematic Liquid Crystals

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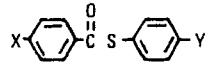
A class of nematic liquid crystals, the *p*-,*p*′-disubstituted phenyl thiolbenzoates, I, are reported.



I

The phenyl thiolbenzoates have higher melting points and higher clearing points than the oxygen analog phenylbenzoates. This increased nematic stability affords the formulation of liquid crystalline systems with high clearing points. The phenyl thiolbenzoates were synthesized by condensation of a benzoyl chloride and thiophenol. The thiophenols were prepared by the alkaline hydrolysis of the corresponding xanthate esters. The results indicate that the phenyl thiolbenzoates show good potential for use in field effect display devices.

INTRODUCTION

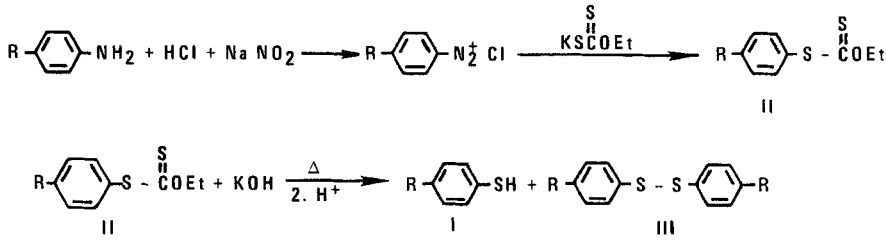
In view of the interest in room temperature nematic materials and in particular their use in a variety of electro-optical applications,[1,2] various different types of compounds that might have liquid crystalline properties suitable for use in display devices have been examined. The Schiff bases[3,4] were among the first and most thoroughly studied systems. The substituted phenylbenzoates[5] and most recently the substituted biphenyls[6,7] have received widespread attention. Both systems are stable under conditions dictated for use in field effect displays, with biphenyls being by far the most stable of any system discovered, and both systems appear to show great promise for use in this multi-million dollar industry.

Structural modifications of known liquid crystalline type materials have been examined. Van Meter and Klanderman[5] examined some phenylbenzoate esters in which the oxygen in a terminal substituent was replaced by sulfur. Their results indicated that sulfur in a terminal substituent sulfide linkage destabilized the nematic mesophase. Castellano[8] also observed this same effect for sulfur containing Schiff bases. He explained this destabilization in terms of the decreased polarity of the alkylthio group. We felt that incorporation of sulfur into the central ester linkage, i.e., a disubstituted phenyl thiolbenzoate, would not destabilize the nematic mesophase, but rather stabilize any mesomorphic tendencies. The decreased polarity of sulfur versus oxygen should lower permanent dipole repulsions between adjacent molecules, and the increased polarizability of the non-bonded *d*-electrons of sulfur over the non-bonded *p*-electrons of oxygen should increase resonance delocalization of these non-bonded electrons reducing electron-electron repulsion between adjacent molecules. Both of these factors should effectively increase the forces involved in holding a compound in a mesogenic state. Additionally, van der Waal's forces increase with increasing molecular weight in a series and this slightly increased attractive force should also serve to further stabilize any mesomorphic tendencies. Indeed, Rheinboldt[9] in studying binary systems of aromatic esters and thiol esters reported that 4′-methylphenyl-4-thiolanisoate had an anisotropic phase from 65.5°C to 73.6°C. A variety of *p*-*p*′-disubstituted phenyl thiolbenzoates have been synthesized in our laboratory and the results show that these compounds are indeed liquid crystalline and do have increased mesomorphic stability over the oxygen analogs.

RESULTS AND DISCUSSION

The acid chlorides, where not commerically available, were synthesized by the Fridel–Crafts acylation of an alkylbenzene using oxalyl chloride.[10]

Where commercially available, 4-substituted thiophenols were obtained and either used as is or vacuum distilled prior to use. The 4-alkylthiophenols, I, were synthesized by the alkaline hydrolysis of the corresponding xanthate esters, II, as outlined in the following schematic.[11]



The major by-product from this reaction is the disulfide, III. Other by-products from these reactions were not characterized. The yield of I after a final distillation using a Nester–Faust NFA-200 spinning band annular still at 7200 r.p.m. and 0.1 to 0.8 mm Hg was from 58% to 81% of theoretical value. The formation of the ethyl S-(4-alkylphenyl) xanthate, II, proceeds smoothly if reaction conditions are carefully controlled. On one occasion, the formation of ethyl S-(4-pentylphenyl) xanthate, flashes of light were observed when the reaction temperature was allowed to exceed 50°C. The hydrolysis of the xanthate ester to I and III proceeds smoothly but care must be exercised in the addition of potassium hydroxide to the warm alcoholic solution of the xanthate such that violent ebullition does not occur. The by-product disulfide, III, can be eliminated by converting it to the mercaptan by refluxing over zinc metal or by reduction using lithium aluminum hydride. The thiophenols synthesized in the indicated manner are not obtained as completely pure products. As detailed in the experimental section, 4-thiopentylphenol and 4-thiopentyloxyphenol were 98.6% and 96.5% pure respectively. Thus, elemental analysis for these compounds are only grossly accurate; however, the phenyl thiolbenzoates synthesized from these mercaptans are easily worked up to give high purity materials. *p*-Pentylphenyl-*p*-ethoxythiolbenzoate synthesized from *p*-pentylthiophenol and *p*-ethoxybenzoyl chloride was obtained 99.92 mole % pure (by DSC) and having an elemental composition very close to its calculated value. Likewise *p'*-pentyloxyphenyl-*p*-heptylthiolbenzoate derived from *p*-pentyloxythiophenol (96.5% pure) and *p*-heptylbenzoyl chloride was found to be 99.58 mole % pure (by DSC) and elemental analysis agreed with calculated values. The impurities present in the synthesized thiophenols do not interfere significantly with the purification of the disubstituted phenyl thiolbenzoates.

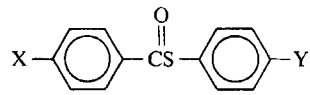
The *p*-,*p'*-disubstituted phenyl thiolbenzoates were synthesized by condensing the corresponding benzoyl chloride and a substituted thiophenol in benzene with a stoichiometric equivalent of pyridine as the acid scavenging agent. The reaction products were purified by recrystallization and/or vacuum distillation.

The results of our work are summarized in Table I. All the phenyl thiolbenzoates synthesized are odorless, colorless compounds, with the exception of some of the nitro substituted compounds, and show no signs of becoming colored on storage under normal conditions. Of the compounds studied thus far, none are nematic at room temperature. One compound, the *p*-,*p'*-di-*n*-butylphenyl thiolbenzoate (compound 3, Table I) was observed to have an enantiotropic nematic phase below room temperature.

Compounds 15, 29, and 34 were all observed to have smectic phases present. Preliminary characterization of the smectic phase for compounds 15 and 34 just below the nematic show it to be smectic A. The other smectic phases have not at the present time been characterized.

TABLE I

p-,*p*'-Disubstituted phenyl thiolbenzoates



Compound	where $X =$	where $Y =$	Purity	ΔT(°C) (nematic range)
1	C_3H_7	C_4H_9	99.14% by DSC	34.2–35.2
2	C_3H_7	C_5H_{11}	99.72% by DSC	[58][a]
3	C_4H_9	C_4H_9	98.97% by DSC	13.9–22.5
4	C_4H_9	C_5H_{11}	Single spot TLC[d]	28.1–33.0
5	C_5H_{11}	C_4H_9	97.9% by DSC	28.0–34.7
6	C_6H_{13}	C_4H_9	Single spot TLC	[28.5]
7	C_6H_{13}	C_5H_{11}	99.73% by DSC	[48.2]
8	H	C_5H_{11}	99.77% by DSC	48.8[b]
9	C_7H_{15}	C_4H_9	99.76% by DCS	34.6–42.6
10	C_7H_{15}	C_5H_{11}	99.45% by DSC	31.6–55.0
11	C_8H_{17}	C_4H_9	99.19% by DSC	[44.9]
12	C_8H_{17}	C_5H_{11}	Single spot TLC	39.6–46.0
13	C_9H_{19}	C_4H_9	Single spot TLC	38.0–44.8
14	C_9H_{19}	C_5H_{11}	99.68% by DSC	39.6–56.4
15	$C_{10}H_{21}$	C_5H_{11}	99.64% by DSC	47.2–52.4[c]
16	CH_3O	C_4H_9	99.87% by DSC	[64.4]
17	CH_3O	C_5H_{11}	99.52% by DSC	64.4–75.0
18	C_2H_5O	C_4H_9	99.85% by DSC	66.9–88.9
19	C_2H_5O	C_5H_{11}	99.96% by DSC	80.5–97.5
20	C_3H_7O	C_4H_9	99.78% by DSC	50.0–68.5
21	C_3H_7O	C_5H_{11}	99.18% by DSC	62.3–79.4
22	C_4H_9O	C_4H_9,	Single spot TLC	50.5–70.3
23	C_4H_9O	C_5H_{11}	99.66% by DSC	60.4–89.9
24	$C_5H_{11}O$	C_4H_9	99.28% by DSC	60.2–69.7
25	$C_5H_{11}O$	C_5H_{11}	99.12% by DSC	63.1–79.4
26	$C_6H_{13}O$	C_5H_{11}	99.31% by DSC	59.9–85.9
27	$C_7H_{15}O$	C_4H_9	99.37% by DSC	56.9–74.0
28	$C_7H_{15}O$	C_5H_{11}	99.18% by DSC	54.3–81.5[c]
29	$C_7H_{15}O$	$C_5H_{11}O$	Single spot TLC	63.0–96.8[c]
30	C_7H_{15}	$C_5H_{11}O$	99.85% by DSC	57.7–70.9
31	$C_7H_{15}O$	NO_2	No purity data	69.0–85.0
32	$C_7H_{15}O$	F	No purity data	[67]
33	$C_8H_{17}O$	C_4H_9	98.55% by DSC	59.1–76.3
34	$C_8H_{17}O$	C_5H_{11}	99.92% by DSC	65.0–87.9[c]
35	C_9H_{19}	CN	Single spot TLC	81.0–85.0
36	C_6H_5	NO_2	Single spot TLC	184–193

[a] [ ] brackets denote a monotropic nematic.

[b] no nematic observed.

[c] contain smectic phases.

[d] TLCs were run on Baker flex IB-F silica gel using two solvent systems: Benzene and 9:1 Benzene/ethyl acetate.

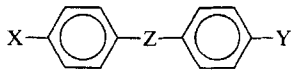
Like phenylbenzoate esters and biphenyls, a comparison of the compounds reported shows that the *p*-alkoxy substituted compounds have higher nematic stabilities, as evidenced by the higher N–I transition temperatures, than the *p*-alkyl substituted phenyl thiolbenzoates.

The mesomorphic stability of the phenyl thiolbenzoates as compared to the analogous phenylbenzoate esters is shown in Table II. Without exception, where transition data is available for analogous compounds, the phenyl thiolbenzoates have higher mesomorphic transition temperatures than the corresponding phenylbenzoates. Of particular interest are compounds 8a, 8b, 9a and 9b. The phenylbenzoate esters (8b and 9b) have not been shown to be nematic, while the corresponding phenyl thiolbenzoates (8a and 9a) are both monotropic nematics and their transitions occur above the isotropic melting points of 8b and 9b respectively.

A plot of temperature versus increasing chain length for the homologous series *p*-alkoxy-*p'*-pentylphenyl thiolbenzoate is shown in Figure 1. The nematic to isotropic transition temperatures show a nice alternating effect.

TABLE II

Comparison of phenylbenzoate vs. phenyl thiolbenzoate esters



Compound	where X =	where Y =	Nematic range (°C) a. Z = —C(=O)—S—	Nematic range (°C) b. Z = —C(=O)—O—	Literature value (°C) b. Z = —C(=O)—O—
1	CH_3O—	C_4H_9	[64.4][a]	[28]	[23][c], [29][d]
2	CH_3O—	C_5H_{11}	64.4–75.0	29–42	29.5–43.5[c]
3	C_2H_5O—	C_5H_{11}	80.5–97.5	[66]	[68][e]
4	C_4H_9O—	C_4H_9	50.5–70.3	[50]	[50][e]
5	C_4H_9O—	C_5H_{11}	60.4–89.9	[61]	[62][e]
6	$C_5H_{11}O$—	C_5H_{11}	63.1–79.4	38–52	40–55[c]
7	C_4H_9	C_5H_{11}	28–33	[9]	[8.5][e]
8	C_6H_{13}	C_4H_9	[28.5]	18 ≠[b]	18 ≠[e]
9	C_6H_{13}	C_5H_{11}	[48.2]	27.3 ≠	—[f]
10	C_6H_5	NO_2	184–193	[155]	—[f]

[a] [ ], brackets denote a monotropic nematic.
[b] ≠, denotes an isotropic transition where no nematic phase has been detected.
[c] Reported transition temperature, Reference 5.
[d] Reported transition temperature, Reference 12.
[e] Reported transition temperature, Reference 13.
[f] Literature reference data not available.

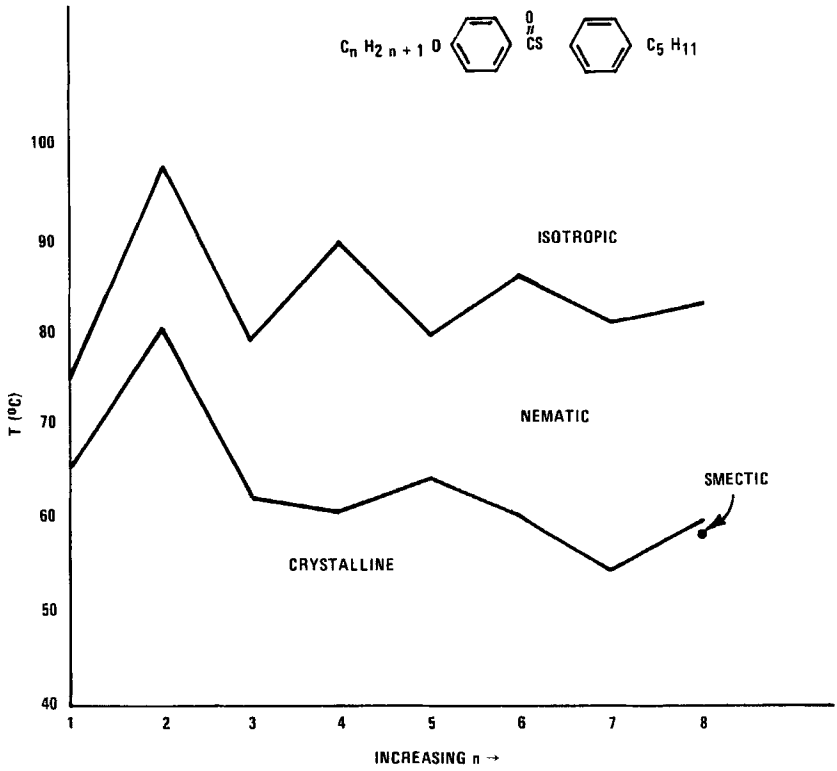


FIGURE 1 Transition temperature versus increasing chain length for the homologous *p*-pentyphenyl-*p'*-alkoxypenylbenzthiolate series. Note the appearance of an enantiotropic spectic phase for $n = 8$.

The compounds with an even number of carbon atoms in the terminal substituent chain have higher N–I transitions than the odd numbered series and the entire series of these compounds show a smooth descension of transition temperatures. No predictable pattern for the crystalline to mesophase transition temperature is apparent other than a gradual decrease. An enantiotropic smectic phase first appears for the *n*-octyloxy compound. On cooling, two additional smectic textures for this compound can be observed. The presence of multiple smectic textures for the octyloxy compound suggested that monotropic smectic textures might be observed for the *n*-heptyloxy and possibly even the *n*-hexyloxy compound. *p*-Heptyloxy-*p'*-pentylphenyl thiolbenzoate (compound 28, Table I) did indeed show a monotropic smectic phase at 35.3°C. The *p*-hexyloxy homolog was not smectogenic.

SUMMARY AND CONCLUSIONS

A variety of *p*-,*p'*-disubstituted phenyl thiolbenzoates have been synthesized and have been shown to be a class of liquid crystalline materials. The phenyl thiolbenzoates, as evidenced by higher crystalline to nematic and nematic to isotropic transition temperatures, have increased mesomorphic stability over the analogous phenylbenzoates.

Some preliminary data suggests that the phenyl thiolbenzoates may be feasible for display applications. The hydrolytic stabilities, in strong base, of some analogous phenyl thiolbenzoates, phenylbenzoates and Schiff bases have been compared.† After 10.0 hours at pH = 10.3 (conc. NaOH/conc. L.X. = 2×10^{-4} M/4×10^{-5} M) in 1:1 acetonitrite/water at 24°C; 49% of the initial *p*-methoxybenzylidene-*p'*-*n*-butylaniline (MBBA) had hydrolyzed, 9% of the *p'*-butylphenyl-*p*-thiolanisoate (compd 1a, Table II) had hydrolyzed, and 7% of the *p'*-pentylphenyl-*p*-anisoate (compd 2b, Table II) had hydrolyzed. Thus the phenyl thiolbenzoates appear to be only slightly less stable towards basic hydrolysis than the analogous phenylbenzoates.

As with other classes of liquid crystalline compounds, the phenyl thiolbenzoates can be combined to provide mixtures with wider nematic ranges than either of the constituent compounds. For example, *p'*-pentylphenyl-*p*-thiolanisoate (compound 17, Table I) (nematic range 64.4°C–75°C) and *p'*-pentylphenyl-*p*-pentyloxythiolbenzoate (compound 25, Table I) (nematic range 63.1°C–79.4°C) can be combined in approximately equal weight proportions to form an eutectic having a nematic range from 42°C to 76°C.

EXPERIMENTAL

Purity of the synthesized thiophenols was determined by gas chromatography using a Varian model 2800 G.C. coupled to an Autolab System I computing integrator. Satisfactory infrared spectra were obtained.

The purities of the *p'*,*p'*-disubstituted phenyl thiolbenzoates were determined by gas chromatography, thin layer chromatography, and/or a computer assisted purity program supplied by the Perkin–Elmer Corp. for use with the DSC-2 differential scanning calorimeter. Transition temperatures were determined using the Perkin–Elmer DSC-2 and thermal microscopy using a Mettler FP5 + 52 recording microfurnace mounted on a Leitz–Wetzlar polarizing microscope. Confirmation of structure was by infrared

† Complete hydrolysis studies will be reported at a later date.

spectra obtained on a Beckman IR-4 infrared spectrophotometer and for a few representative compounds elemental analysis were obtained and were found to be in close agreement with calculated values.

As the synthesis and purification of the compounds reported herein are basically similar, detailed experimental data will only be given for a few characteristic compounds.

Acid chlorides

p-Octylbenzoyl chloride Oxalyl chloride (73.5 gm 0.579 mole) was added dropwise to a cooled suspension of $AlCl_3$ (77.0 gm, 0.579 mole) in 600 ml methylene chloride at 0°C. Over a two hour period, phenyloctane (100.0 gm, 0.526 mole) was added to the above suspension such that the temperature was maintained from -5 to -2°C. After stirring for one additional hour at 0°C, the resulting mixture was poured over 100 gm ice to which 50 ml conc. HCl had previously been added. The mixture was stirred vigorously until the ice melted, then the aqueous phase was separated off and discarded. The organic phase was dried over molecular sieves (Linde type 4-A) and the solvent removed under reduced pressure using a rotoevaporator. Vacuum distillation afforded 100.1 gm (75.2%) of colorless product: b.p. 118–120°C at 0.15 mm Hg; ν_{max}^{neat} 1779, 1210, and 880 cm^{-1}.

Thiophenols

p-Pentylthiophenol Freshly distilled *p*-pentylaniline (70.7 gm, 0.25 mole) was slowly added to a solution of 50 ml conc. HCl and 100 gm ice. The suspension was cooled to less than 0°C by immersing in an ice-salt bath and over a period of one hour a cold solution of sodium nitrite (18.8 gm, 0.267 mole) dissolved in 60 ml water was added.

The above formed diazonium salt solution was slowly transferred to a warmed solution of potassium ethyl xanthate (46.9 gm, 0.29 mole) (Eastman technical grade) dissolved in 200 ml water at such a rate that the temperature was maintained from 40 to 45°C. The oily xanthate was then extracted using two 50 ml portions of ether. The ether solution was washed with 10% NaOH (1 × 50 ml) and then with water to pH7. The ether was stripped off on the rotoevaporator and the resulting oil was dissolved in 175 ml of 95% ethanol. The solution was brought to a gentle boil, the source of heat removed and a solution of KOH (56.0 gm, 1.0 mole) dissolved in 200 ml ethanol was added at a rate sufficient to keep the solution refluxing. After refluxing for an additional 14 hr, the solution was concentrated to approximately 30 ml volume. The resulting slurry was dissolved in 200 ml hot water, acidified with conc. H_2SO_4, and extracted with ether. The ether was removed on the roto-

evaporator, 1.0 gm zinc was added and refluxed for one hour. The zinc was filtered off and the product vacuum distilled to afford 36.0 gm (81%) colorless fluid: b.p. 86°C at 0.8 mm Hg; 98.62% pure by G.C.; ν_{max}^{neat} 2570, 1100, and 915 cm^{-1}.

Anal. Calculated for $C_{11}H_{16}S$; C, 73.27; H, 8.95; S, 17.78.
Found: C, 74.17; H, 9.06; S, 19.04.

p-Pentyloxythiophenol Starting with freshly distilled *p*-pentyloxyaniline, *p*-pentyloxythiophenol was synthesized in exactly the same manner as the previously described *p*-pentylthiophenol with the exception that the resulting product was not refluxed over zinc prior to distillation. The two products received after distillation using the spinning band still were:

p-pentyloxythiophenol; yield = 57%, 96.53% pure by G.C., b.p. 67°C at 0.10 mm Hg; ν_{max}^{neat} 2570, 1240, 1175, 910, and 820 cm^{-1}.

Anal. Calculated for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33
Found: C, 66.58; H, 8.16; S, 16.87.

and

p-pentyloxyphenyl disulfide; yield = 38%, 94.6% pure by G.C., b.p. 91°C at 0.10 mm Hg; ν_{max}^{neat} 1240, 1175, and 810 cm^{-1}.

Anal. Calculated for $C_{22}H_{30}O_2S_2$: C, 70.54; H, 8.07; S, 17.12.
Found: C, 69.05; H, 8.72; S, 15.43.

p-,p'-Disubstituted phenyl thiolbenzoates

p'-Pentylphenyl-p-ethoxythiolbenzoate *p*-Ethoxybenzoyl chloride (2.02 gm, 0.011 mole) was added to a solution of *p*-pentylthiophenol (1.80 gm, 0.01 mole) and pyridine (0.8 ml, 0.01 mole) in 25 ml benzene. The mixture was heated to 70°C and stirred for 48 hr. The reaction was then transferred to a 250 ml separatory funnel using a 100 ml benzene rinse and washed successively with water (2 × 100 ml), 3% phosphoric acid (2 × 100 ml), water (1 × 100 ml), saturated sodium bicarbonate (2 × 100 ml), and water (2 × 100 ml). After drying over molecular sieves (Linde type 4A) the solution was concentrated to dryness and the resultant colorless crystals were recrystallized two times from ether-petroleum ether (30–60°) to afford 1.7 gm (52%) of fine colorless crystals: m.p. 80.0°C, c.p. 97.5°C; 99.92 mole % pure by DSC; ν_{max}^{KBr} 1675, 1265, 1210, 1175, 1040, and 910 cm^{-1}.

Anal. Calculated for $C_{20}H_{24}O_2S$: C, 73.13; H, 7.36; 0, 9.74; S, 9.77
Found: C, 73.17; H, 7.42; 0, 9.71; S, 9.73.

p'-Pentyloxyphenyl-p-heptythiolbenzoate *p*-Heptylbenzoyl chloride (2.52 gm, 0.01 mole) and triethyl amine (1.39 ml, 0.01 mole) were added to a

solution of *p*-pentyloxythiophenol (1.96 gm, 0.01 mole) dissolved in 25 ml benzene. The reaction was heated to 40°C and stirred for 24 hours. At the end of this time the reaction mixture was transferred to a 250 ml separatory funnel using a 100 ml benzene rinse and washed with water (2 × 100 ml), 3% phosphoric acid (2 × 100 ml), water (1 × 100 ml), saturated sodium bicarbonate (2 × 100 ml), water (1 × 100 ml), and dried over anhydrous magnesium sulfate. After removing the solvent on the rotoevaporator, the product was recrystallized two times from ethyl acetate to afford 1.3 gm (32%) of fine colorless crystals: m.p. 57.7°C, c.p. 70.9°C; 99.58 mole % pure by DSC; ν_{max}^{neat} 1680, 1255, 1220, 1175, and 905 cm^{-1}.

Anal. Calculated for $C_{25}H_{34}O_2S$: C, 75.33; H, 8.60; S, 8.04
Found: C, 75.21; H, 8.59; S, 8.41.

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