Table II. ^{13}C NMR Spectral Data for 1 and 2[c]

Carbon atom	Multiplicity[a]	δc 1	δc 2
15	s	168.5	168.8
13	s	152.4	153.7
12	s	149.1	149.4
9	s	143.0	141.9
1	s	137.4	137.3
8	d	136.9	136.8
2	s	130.3	130.8
7	d	130.1	130.1
10	d	121.7	122.4
14	d	118.1	155.1
11	d	113.0	107.5
5	t	39.5	39.6
6	s	34.2	34.2
3	t	33.0	33.2
17, 18[b]	q	28.9	28.9
16	q	21.7	21.7
4	t	19.1	19.2
20	q	15.7	12.8
19	q	12.3	11.6

[a] Single frequency off-resonance multiplicity. [b] Two-carbon peak. [c] See 1 for numbering of carbon atoms.

no hydrogens), thus conclusively confirming the structure of **2**.

The ^{13}C NMR spectral data for compounds **1** and **2** are given in Table II. The chemical shifts for these two compounds are very similar to those of *all-trans*-retinoic acid and its isomers,[10] and the majority of peaks can be readily assigned. However, there are three carbon atoms—carbon atoms 10, 11, and 12—which differ significantly in chemical shift from those of the retinoic acids and cannot be assigned by direct comparison. The unassigned carbon atoms due to C-10 and C-11 are found in the spectral region from ~107 to 123 ppm. In both **1** and **2**, the chemical shifts of C-11 would be expected at higher field than those of C-10, since C-11 is closer to the lactone ring. In addition, a larger chemical shift difference would also be expected for C-11 than for C-10 in going from **1** to **2**. The chemical shifts of C-10 and C-11 in *all-trans*-retinal occur at 129.4 and 132.4 ppm, respectively.[10] Thus, the peaks found for **1** and **2** at 113.0 and 107.5 ppm were assigned to C-11 (upfield shift of ~21 ppm; Δδ 5.5 ppm); the peaks at 121.7 and 122.4 ppm were assigned to C-10 (upfield shift of ~9 ppm; Δδ 0.7 ppm). Because it is directly bonded to oxygen, C-12 should exhibit a large downfield shift in both compounds when compared to the retinoic acids; the downfield shift should be approximately the same in both compounds. Thus, C-12 is assigned to the carbon atoms at 149.1 and 149.4 ppm for **1** and **2**, respectively.

Experimental Section

Melting points were determined on a Kofler micro hot stage and are corrected values. The ^{13}C NMR spectra were recorded on 100 mg of each compound in deuteriochloroform solution on a Varian XL-100 NMR spectrometer at 25.2 MHz in the Fourier transform mode. The spectra were obtained using a 5000-Hz sweep width and an 8K data table. Elemental and spectral analyses and x-ray structure determinations were carried out by the Physical Chemistry Department, Hoffmann-La Roche Inc.

(2,5-Dihydro-3-methyl-5-oxofuran-2-yl)triphenylphosphonium Bromide (5c). A mixture of 13.28 g (0.135 mol) of the butenolide **5a**,[7] 26.4 g (0.149 mol) of *N*-bromosuccinimide, and 200 ml of carbon tetrachloride was heated to the reflux with a light source for 2 h. The mixture was allowed to cool and was filtered; the filtrate was concentrated in vacuo to give 23.3 g (0.131 mol) of crude 4-bromobutenolide **5b**. Without further purification, this was combined with 38 g (0.145 mol) of triphenylphosphine and 250 ml of benzene and heated to the reflux for 5 h. The mixture was allowed to cool to room temperature overnight and then was filtered to give 41.4 g (0.094 mol) of phosphonium salt **5c**. This material was used in the next step without further purification.

(*E*)-4-Methyl-5-[5-(2,6,6-trimethylcyclohexen-1-yl)-3-methyl-2(*E*),4(*E*)-pentadienylidene]-2(5*H*)-furanone (1). To a cooled (5 °C) suspension of 17.2 g (78.2 mmol) of C_{15} aldehyde **4**, 41.4 g (94 mmol) of phosphonium salt **5c**, and 150 ml of dry dimethylformamide, 2.26 g (94 mmol) of sodium hydride (56.6% in mineral oil) was added. After the addition was completed, the reaction mixture was stirred at room temperature for 2 h, then heated to 60 °C for 16 h. The mixture was cooled and then poured into 500 ml of ice water. The aqueous layer was saturated with sodium chloride and extracted with three 250-ml portions of chloroform. The combined extract was washed twice with saturated sodium chloride solution and dried over sodium sulfate. Evaporation of the solvent gave 32.6 g of an oil, which was purified by chromatography on 900 g of silica gel packed in hexane. Elution with hexane containing 2% ether, and gradually increasing to 15% ether, gave 5.5 g of an isomeric mixture. This was purified by repeated recrystallization from pentane to give 2.4 g (10.2%) of the less polar furanone **1** as yellow crystals: mp 129–137 °C; NMR (CCl_4) δ 1.04 (s, 6 H), 1.71 (s, 3 H), 2.01 (s, 3 H), 2.40 (s, 3 H), 5.88 (m, 1 H), 6.1 (d, J = 16 Hz, 1 H), 6.3 (d, J = 16 Hz, 1 H), 6.37 (d, J = 12 Hz, 1 H), and 6.60 (d, J = 12 Hz, 1 H); mass spectrum *m/e* 298 (M^+), 283, 265, and 255; uv λ_{max} (2-propanol) (ε) 388 nm (39 130); ir ($CHCl_3$) 1747, 1587, and 1574 cm^{-1}. The material was found to be 94.5% isomerically pure by liquid chromatographic analysis.

Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.54; H, 8.96.

(*Z*)-4-Methyl-5-[5-(2,6,6-trimethylcyclohexen-1-yl)-3-methyl-2(*E*),4(*E*)-pentadienylidene]-2(5*H*)-furanone (2). The mother liquors from the above pentane recrystallization were combined and stored at −20 °C for 3 days. The resulting crystals were filtered and the two crystal forms were separated manually. Repeated recrystallization of the lower melting, more polar substance from cold pentane gave 350 mg of **2** as yellow crystals: mp 90–95 °C; NMR (CCl_4) δ 1.02 (s, 6 H), 1.21 (s, 3 H), 1.99 (s, 3 H), 2.18 (s, 3 H), 5.81 (m, 1 H), 6.01 (d, J = 12 Hz, 1 H), 6.24 (s, 2 H), and 6.53 (d, J = 12 Hz, 1 H); mass spectrum *m/e* 298 (M^+), 283, and 265; uv λ_{max} (2-propanol) (ε) 385 nm (26 820) and 242 (7900); ir ($CHCl_3$) 1750 and 1575 cm^{-1}.

Anal. Calcd for $C_{20}H_{26}O_2$: C 80.50; H, 8.78. Found: C, 80.60; H, 8.79.

Registry No.—**1**, 60305-11-5; **2**, 10035-29-7; **3**, 55177-16-7; **4**, 3917-41-7; **5a**, 6124-79-4; **5b**, 60270-03-3; **5c**, 60270-04-4; triphenylphosphine, 603-35-0.

Supplementary Material Available. Tables of positional and thermal parameters for the structure of **1** (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Compounds **1** and **2** are named as derivatives of 2(5*H*)-furanone. However, because of their relationship to retinoic acid, this numbering system has been employed in this paper for purposes of discussion.
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Carbohydrate Thio Ortho Esters. Synthesis and Characterization

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Carbohydrate ortho esters have been used extensively during the last 10 years for synthesis of 1,2-trans glycosides.[1]

Table I. Yield and Product Composition for the Formation of Thio Ortho Esters (cf. Scheme I)

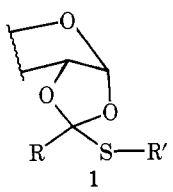
Registry no.	Starting material[a] (configuration)	Yield[b] (%)	Product composition[c] (exo/endo, %)
572-09-8	D-gluco	**2** (79)	71/29
3068-32-4	D-galacto	**3** (72)	70/30
3068-31-3	D-xylo	**4** (77)	80/20
4753-07-5	D-"lacto"	**5** (55)	100/0
21085-72-3	D-glucurono[d]	**6** (89)	56/44

[a] Per-O-acetylated α-D-glycopyranosyl bromide. [b] Isolated product. [c] Determined from NMR integrals. [d] Methyl ester.

Table II. ^{13}C NMR Chemical Shifts (ppm, Me_4Si) for the Exo (2a) and Endo (2b) Gluco Thio Ortho Esters and the β-Thioglucoside (2c)

Compd	C_1	C_{2-6}	CH_3CO	CH_3CO	Arom C	CH_3Ph	CH_3CS	CH_3CS
Exo (**2a**)	97.32	73.21	20.78	170.52	139.11	21.26	26.46	117.93
		69.80		169.55	135.62			
		68.26		169.14	129.70			
		66.88			128.24			
		62.98						
Endo (**2b**)	97.87	75.53	20.63	170.63	139.45	21.28	28.34	118.25
		72.20		169.74	136.36			
		70.66		169.50	129.70			
		67.98			127.35			
		62.21						
Glucoside (**2c**)	85.79	75.73	20.61	170.44	138.70	21.18		
		74.02		170.03	133.76			
		69.88		169.14	129.62			
		68.18			127.50			
		62.09						

Thio ortho esters (**1**), however, have not been reported although they should have potential in carbohydrate synthesis (glycoside synthesis, protective group, reduction to acetals, oxidation to sulfoxides and sulfones, S-alkylation, transformation by heavy metal ions, etc.).



1

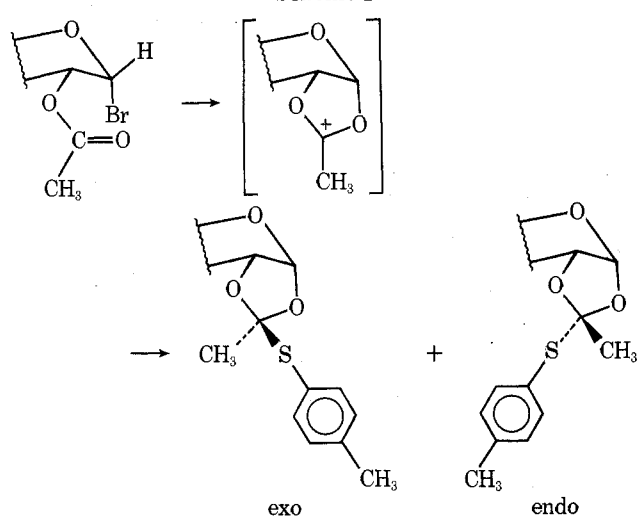
I now wish to report the synthesis and characterization of *p*-methylthiophenyl ortho esters[2] of some representative mono- and disaccharides (peracetylated). The synthesis consists of heating equimolar amounts of the appropriate acetobromo sugar, *p*-methylthiophenol, and 2,4,6-trimethylpyridine in nitromethane. Chromatography of the reaction mixture gave the thio ortho esters in good yields together with small amounts of di-*p*-methyl phenyl disulfide and β-thioglycoside (see Table I). The mechanism of the reaction probably involves initial solvent attack[3] on the acetobromo sugar followed by acetoxonium ion formation. This will then react with the thiol to give the thio ortho ester (see Scheme I).

A mixture of exo and endo isomers was obtained using acetobromo monosaccharides but only the exo compound was formed from acetobromo lactose. Probably the galactose residue hinders thiol attack at the endo side of the intermediate acetoxonium ion.

In order to determine the structures of these compounds, the gluco isomers (exo and endo thio ortho esters and the β-thioglucoside) were isolated in pure (NMR) form and investigated by spectroscopic methods.

The ^1H NMR spectra showed the following significant features: a low-field (ca. 5.7 ppm) rough doublet with a splitting of ca. 5 Hz for the thio ortho ester anomeric protons.

Scheme I



Further, *C*-methyl group singlets (1.82 and 1.63 ppm) were found for the exo and endo thio ortho esters (absent for the β-thioglucoside). This is in accordance with normal ortho esters.[4]

The ^{13}C NMR spectra of the thio ortho esters (see Table II) showed high-field signals for the *C*-methyl group carbons and low-field signals for the quaternary carbons of the ortho ester group. These signals were absent with the β-thioglucoside.

All the thio ortho esters reported here showed a low-intensity molecular ion peak in the mass spectrum. Other significant features were a strong M − 123 peak for the acetoxonium ion (cf. Scheme I) and base peak at 169 mass units.

Since sulfur is less basic than oxygen, one could expect thio ortho esters of the present type to be more acid stable than normal ortho esters. The latter are completely hydrolyzed by dilute sulfuric acid in acetone within ca. 30 min.[3] With the thio ortho esters, approximately 50% hydrolysis occurred after 3 h under the same conditions.

The relative hydrolytic stability of this new type of compound and the possibility of utilizing the unique properties of sulfur for selective transformations suggest that thio ortho esters should be versatile intermediates in synthetic sugar chemistry.

Experimental Section

Melting points are uncorrected. Ir spectra were run as KBr tablets. ^1H and ^{13}C NMR spectra were run in $CDCl_3$ (Me_4Si) on JEOL PMX-60 and JEOL FX-60 spectrometers, respectively. Mass spectra were run on a Varian MAT 311 spectrometer.

General Procedure for Preparation of the Thio Ortho Esters. The appropriate acetobromo sugar (2.5 mmol) and *p*-methylthiophenol (2.5 mmol, recrystallized from petroleum ether) were dissolved in dry nitromethane (3 ml) containing 2,4,6-trimethylpyridine (2.55 mmol). The solution was stirred (magnet) under N_2 at 50 °C for ~5 h (compound **6**, 15 h). The reaction was followed by TLC (SiO_2, ethyl acetate–light petroleum). 2,4,6-Trimethylpyridinium bromide was formed as a white precipitate. The reaction mixture was cooled and ether (10 ml) was added to complete the precipitation. Filtration and evaporation of the filtrate gave a colorless syrup which was chromatographed on silica (100 g, Merck Kieselgel 60, 0.063–0.200 mm) with ethyl acetate–light petroleum as eluent (1:2 for monosaccharide and 1:1 for disaccharide thio ortho esters). This gave as the first fraction a few milligrams of **di-*p*-methyl phenyl disulfide** [ir 1490, 798 cm^{-1}; NMR δ 7.34, 7.04 (rough AB q, 4 H each, J_{AB} = 8.3 Hz, aromatic H), 2.27 ppm (s, 6 H, CH_3Ph); mass spectrum *m/e* (rel intensity) 246 (M^+, 100, base peak), 123 (80). Anal. Calcd for $C_{14}H_{14}S_2$: mol wt, 246.0537. Found: mol wt, 246.0541] followed by a second fraction of pure exo thio ortho ester and a third fraction of exo plus endo thio ortho esters (for monosaccharides). Trace amounts of the thioglycosides could be isolated in some cases from a fourth fraction (verified for the gluco compound). The composition (exo/endo) was determined from NMR integrals of the CH_3CS signals (see Table I). Yields are not optimized.

3,4,6-Tri-*O*-acetyl-1,2-*O*-*p*-methylthiophenoxyethylidene-α-D-glucopyranose (2). Yield 79% (exo plus endo isomer; see Table I).

Exo Isomer (2a): syrup;[6] $[\alpha]^{25}_{578}$ +78.9° (*c* 0.735, $CHCl_3$); ir 1750, 810 cm^{-1}; NMR δ 7.41, 7.15 (rough AB q, 2 H each, J_{AB} = 7.8 Hz, aromatic H), 5.77 (d, 1 H, 5.0 Hz splitting, OCHO), 3.76–5.35 (m, 6 H, OCH), 2.36 (s, 3 H, CH_3Ph), 2.15, 2.08 (s, 9 H, CH_3COO), 1.82 ppm (s, 3 H, CH_3CS); ^{13}C NMR, see Table II; mass spectrum *m/e* (rel intensity) 454 (M^+, 0.3, $C_{21}H_{26}O_9S$), 331 (70), 271 (6), 229 (6), 211 (7), 187 (6), 169 (100, base peak).

Anal. Calcd for $C_{14}H_{19}O_9$: mol wt, 331.1029. Found: mol wt, 331.1029 ($M - C_7H_7S$).

Endo Isomer (2b). Rechromatography of the exo/endo mixture gave the pure endo compound (**2b**): syrup; $[\alpha]^{25}_{578}$ +107.9° (*c* 0.410, $CHCl_3$); ir 1755, 810 cm^{-1}; NMR δ 7.56, 7.16 (rough AB q, 2 H each, J_{AB} = 8.1 Hz, aromatic H), 5.69 (d, 1 H, 5.6 Hz splitting, OCHO), 4.00–5.80 (m, 6 H, OCH), 2.37 (s, 3 H, CH_3Ph), 2.09, 2.05 (s, 9 H, CH_3COO), 1.63 (s, 3 H, CH_3CS); ^{13}C NMR, see Table II; mass spectrum *m/e* (rel intensity) 454 (M^+, 0.06, $C_{21}H_{26}O_9S$), 331 (8), 271 (6), 229 (3), 211 (8), 187 (6), 169 (100, base peak).

Anal. Calcd for $C_{14}H_{19}O_9$: mol wt, 331.1029. Found: mol wt, 331.1028 ($M - C_7H_7S$).

***p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (2c):** mp 116–117 °C; $[\alpha]^{24}_{578}$ −19.8° (*c* 2.90, $CHCl_3$) [lit.[5] mp 118 °C; $[\alpha]_D$ −21° (*c* 2.0, $CHCl_3$)]; ir 1748, 919, 820, 810 cm^{-1}; NMR δ 7.38, 7.12 (rough AB q, 2 H each, J_{AB} = 8.0 Hz, aromatic H), 3.51–5.43 (m, 7 H, OCH), 2.34 (s, 3 H, CH_3Ph), 2.07 (s, 6 H, CH_3COO), 2.00, 1.97 ppm (s, 3 H each, CH_3COO); mass spectrum *m/e* (rel intensity) 454 (M^+, 0.1, $C_{21}H_{26}O_9S$), 331 (35), 271 (9), 229 (3), 211 (6), 187 (3), 169 (100, base peak).

Anal. Calcd for $C_{14}H_{19}O_9$: mol wt, 331.1029. Found: mol wt, 331.1026 ($M - C_7H_7S$).

3,4,6-Tri-*O*-acetyl-1,2-*O*-*p*-methylthiophenoxyethylidene-α-D-galactopyranose (3). Yield 72% (exo plus endo isomer; see Table I).

Exo Isomer: syrup; $[\alpha]^{25}_{578}$ +118.5° (*c* 0.287; $CHCl_3$); ir 1757, 810 cm^{-1}; NMR δ 7.41, 7.13 (rough AB q, 2 H each, J_{AB} = 8.0 Hz, aromatic H), 5.85 (d, 1 H, 5 Hz splitting, OCHO), 4.00–5.46 (m, 6 H, OCH), 2.35 (s, 3 H, CH_3Ph), 2.09, 2.06, 2.03 (s, 3 H each, CH_3COO), 1.77 ppm (s, 3 H, CH_3CS); mass spectrum *m/e* (rel intensity) 454 (M^+, 0.1, $C_{21}H_{26}O_9S$), 331 (59), 271 (6), 229 (4), 211 (6), 187 (3), 169 (100, base peak).

Anal. Calcd for $C_{14}H_{19}O_9$: mol wt, 331.1029. Found: mol wt, 331.1020 ($M - C_7H_7S$).

Endo Isomer: NMR δ 1.66 ppm (s, 3 H, CH_3CS).

3,4-Di-*O*-acetyl-1,2-*O*-*p*-methylthiophenoxyethylidene-α-D-xylopyranose (4): yield 77% (exo plus endo isomer; see Table I).

Exo Isomer: syrup; $[\alpha]^{25}_{578}$ +71.8° (*c* 0.490, $CHCl_3$); ir 1749, 810 cm^{-1}; NMR δ 7.38, 7.10 (rough AB q, 2 H each, J_{AB} = 7.6 Hz, aromatic H), 5.58 (d, 1 H, 4.4 Hz splitting, OCHO), 3.37–5.32 (m, 5 H, OCH), 2.31 (s, 3 H, CH_3Ph), 2.08, 2.00 (s, 3 H each, CH_3COO), 1.77 ppm (s, 3 H, CH_3CS); mass spectrum *m/e* (rel intensity) 382 (M^+, 0.1, $C_{18}H_{22}O_7S$), 259 (30), 246 (17) 217 (20), 199 (29), 170 (20), 157 (74), 149 (55), 128 (76), 124 (40), 115 (75), 97 (100, base peak).

Anal. Calcd for $C_{11}H_{15}O_7$: mol wt, 259.0818. Found: mol wt, 259.0809 ($M - C_7H_7S$).

Endo Isomer: NMR δ 1.59 ppm (s, 3 H, CH_3CS).

3,6-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1,2-*O*-*p*-methylthiophenoxyethylidene-α-D-glucopyranose (5): yield 55% (pure exo isomer; see Table I). Recrystallization from ethanol gave an analytical sample: mp 142–143 °C; $[\alpha]^{25}_{578}$ +47.5° (*c* 1.12, $CHCl_3$); ir 1752, 810 cm^{-1}; NMR δ 7.44, 7.20 (rough AB q, 2 H each, J_{AB} = 8.0 Hz, atomatic H), 5.73 (d, 1 H, 5.0 Hz splitting, OCHOCS), 3.69–5.66 (m, 13 H, OCH), 2.37 (s, 3 H, CH_3Ph), 2.17, 2.10, 2.06, 1.96 (s, 18 H, CH_3COO), 1.83 ppm (s, 3 H, CH_3CS); mass spectrum *m/e* (rel intensity) 742 (M^+, 0.05, $C_{33}H_{42}O_{17}S$), 619 (7), 576 (4), 559 (8), 516 (2), 499 (1), 457 (3), 331 (80), 317 (6), 288 (21), 271 (10), 229 (12), 211 (31), 169 (100, base peak).

Anal. Calcd for $C_{26}H_{35}O_{17}$: mol wt, 619.1873. Found: mol wt, 619.1926 ($M - C_7H_7S$). Calcd for $C_{33}H_{42}O_{17}S$: C, 53.4; H, 5.7; S, 4.3. Found: C, 53.1; H, 5.9; S, 4.1.

Methyl 3,4-Di-*O*-acetyl-1,2-*O*-*p*-methylthiophenoxyethylidene-α-D-glucopyranuronate (6). Reaction time was 15 h; yield 89% (exo plus endo isomer; see Table I).

Exo Isomer: syrup; $[\alpha]^{25}_{578}$ +55.7° (*c* 0.445; $CHCl_3$); ir 1752, 827, 810 cm^{-1}; NMR δ 7.37, 7.11 (rough AB q, 2 H each, J_{AB} = 8.0 Hz, aromatic H), 5.84 (d, 1 H, 5.0 Hz splitting, OCHO), 4.16–5.36 (m, 4 H, OCH), 3.75 (s, 3 H, OCH_3), 2.36 (s, 3 H, CH_3Ph), 2.12, 2.06 (s, 3 H each, CH_3COO), 1.83 ppm (s, 3 H, CH_3CS); mass spectrum *m/e* (rel intensity) 440 (M^+, 0.1, $C_{20}H_{24}O_9S$), 317 (7), 259 (24), 257 (11), 199 (24), 197 (8), 157 (53), 155 (59), 97 (100, base peak).

Anal. Calcd for $C_{13}H_{17}O_9$: mol wt, 317.0872. Found: mol wt, 317.0893 ($M - C_7H_7S$).

Endo Isomer: NMR δ 1.61 ppm (s, 3 H, CH_3CS).

Acknowledgments. I am grateful to Birgit Boman for technical assistance and to Lennart Holmquist for running the mass spectra.

Registry No.—**2a**, 60426-93-9; **2b**, 60410-57-3; **2c**, 28244-94-2; *exo*-**3**, 60410-58-4; *endo*-**3**, 60439-00-1; *exo*-**4**, 60410-59-5; *endo*-**4**, 60410-60-8; *exo*-**5**, 60410-61-9; *exo*-**6**, 60410-62-0; *endo*-**6**, 60410-63-1; *p*-methylthiophenol, 106-45-6; 2,4,6-trimethylpyridine, 108-75-8; 2,4,6-trimethylpyridinium bromide, 60410-64-2; di-*p*-methylphenyl disulfide, 103-19-5.

References and Notes

(1) G. Wulff and G. Röhle, *Angew. Chem.*, **86**, 173 (1974).
(2) *p*-Methylthiophenol was chosen for several reasons: it is easily visualized on TLC plates by uv irradiation, the smell is quite tolerable, making its use outside a hood possible, and it can be easily purified by recrystallization from petroleum ether.
(3) N. K. Kochetkov, A. J. Khorlin, and A. F. Bochkov, *Tetrahedron*, **23**, 693 (1967).
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(6) **Note Added in Proof.** Crystals were obtained after several months: mp 115–115.5 °C (from EtOH); $[\alpha]^{25}_{578}$ +85.9° (*c* 0.66, $CHCl_3$).