corresponding selenonesters and in refrigeration there is no change after 6 months.

Experimental Section

General. Proton magnetic resonance spectra were determined with a Varian T-60 spectrometer using tetramethylsilane as an internal standard. A Beckman IR-20A spectrophotometer was used for IR spectra. Microanalyses were performed by CNRS (Service Central de Microanalyse, 94 Thiais, France) and Dornis U. Kolbe, Hohenweg 17, West Germany.

Aliphatic and Aromatic Imido Esters. The above-mentioned compounds were obtained by the method of Reynaud and Moreau.[5]

General Procedure for Synthesis of Aliphatic and Aromatic Selenonesters. The following description for the conversion of imido esters to selenonesters (Table I, 1) may be considered general. A solution of 8.7 g (0.1 mol) of ethyl acetimidate, 30 mL of dry pyridine, and 10 mL of triethylamine in a 100-mL round bottom flask is cooled to −30 °C. About 25 g (0.3 mol) of anhydrous hydrogen selenide (hydrogen selenide is generated from aluminum selenide by addition of water and passed through the calcium chloride tube) is passed through the solution in 30 min at −30 to −20 °C. The flask temperature is allowed to come to 0 °C and immediately poured into 200 mL of ice water. The mixture is extracted with three 50-mL portions of ether. The extracts are combined and treated with diluted hydrochloric acid and washed with water. The ether solution is dried over anhydrous sodium sulfate, concentrated, and distilled to afford 4 g of *O*-ethyl selenoacetate (26%), bp 129 °C.

General Method for Synthesis of N-Monoalkyl or Aryl Aliphatic Selenoamides. The following preparation of *N*-*p*-bromophenylselenoacetamide (Table II, **10**) will serve as general procedure for the preparation of the above-mentioned selenoamides. To 0.96 g (0.04 mol) of magnesium turnings covered with 20 mL of anhydrous diethyl ether in the usual Grignard apparatus, a solution of 4.36 g (0.04 mol) of ethyl bromide in diethyl ether was added dropwise. A solution of 6.88 g (0.04 mol) of *p*-bromoaniline in anhydrous diethyl ether was added dropwise during 30 min, at such a rate that the mixture refluxed. To the resulting suspension, a solution of 3.02 g (0.02 mol) of *O*-ethyl selenoacetate in diethyl ether was added at once. After the addition was completed, the mixture was refluxed 1 h, cooled, and poured into 400 mL of ice water. The reaction mixture was treated with dilute hydrochloric acid. The mixture was extracted with three 50-mL portions of ether. The combined ether phases were washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent leaves a solid which after recrystallization from benzene–petroleum ether gave 4.54 g (82%) of **10**, mp 156 °C. The solid-substituted selenoamides listed in Table II were recrystallized from benzene–petroleum ether to afford analytically pure products.

The N-monoalkyl-substituted aliphatic selenoamides were prepared in dipropyl ether.

General Procedure for Synthesis of *N,N*-Dialkyl Aliphatic Selenoamides. The following description for the preparation of *N,N*-diethylselenopropionamide (Table II, **13**) may be considered general. To 3.30 g (0.02 mol) of *O*-ethyl selenopropionate, a solution of 2.19 g (0.03 mol) of diethylamine in 5 mL of anhydrous ethanol was added. After 15 days, the alcohol solution was fractionated to give 2.69 g (70%) of **13**, bp 122 °C (7 mmHg).

Registry No.—Ethanimidic acid ethyl ester, 1000-84-6; propanimidic acid ethyl ester, 1070-17-3; butanimidic acid ethyl ester, 998-97-0; isopropylimidic acid ethyl ester, 1069-52-9; pentanimidic acid ethyl ester, 999-09-7; hexanimidic acid ethyl ester, 1001-25-8; benzenethanimidic acid ethyl ester, 4971-77-1; benzenecarboximidic acid ethyl ester, 825-60-5; benzenecarboximidic acid 4-methyl ethyl ester, 827-71-4; H_2Se, 7783-07-5; *O*-ethyl selenoisohexanoic ester, 62448-97-9; magnesium, bromo(4-bromobenzenaminato), 58655-99-5; magnesium, bromo(4-methylbenzenaminato), 58655-94-0; magnesium, bromo(4-ethoxybenzenaminato), 62448-95-7; diethylamine, 109-89-7; magnesium, bromo(4-methoxybenzenaminato), 58655-97-3; magnesium, bromo(isopentanaminato), 62448-96-8.

References and Notes

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Reaction of Methylmagnesium Iodide with Methyl Propiolate. A Correction

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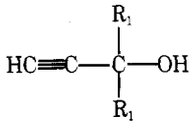
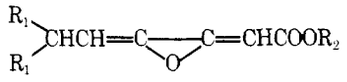
Rhinesmith[1] has recently reported the reaction of methylmagnesium iodide or ethylmagnesium bromide with methyl or ethyl propiolate. Beside the expected acetylenic carbinol **1** (R_1 = CH_3 or C_2H_5) resulting from the addition of 2 mol of Grignard reagent to the ester function, a higher boiling, labile compound was found to which the structure of a doubly unsaturated epoxy ester **2** (R_1 = CH_3 or C_2H_5; R_2 = CH_3 or C_2H_5)

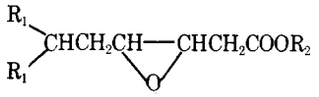


1



2

was assigned based on a combustion analysis, the uptake of 2 mol of hydrogen on catalytic hydrogenation, the IR spectrum, and negative tests for the functional groups –HC=O, >C=O, and –C≡CH. In each case these compounds presumed to have structure **2** were reduced to the alleged saturated β,γ-epoxy esters **3**, which on treatment with methanolic



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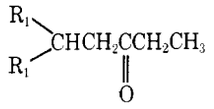
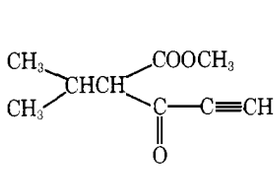


4

potassium hydroxide gave the corresponding ethyl ketones **4** (R_1 = CH_3 or C_2H_5) identified with authentic material. The isolation of a monoepoxide of a 1,2,3-triene such as **2** from a Grignard reaction is unexpected in view of the known instability of epoxides of simple allenes.[2] We therefore repeated the reaction of excess methylmagnesium iodide with methyl propiolate under the conditions described by Rhinesmith[1] while slightly modifying the workup to minimize secondary reactions. VPC analysis of the crude product showed the presence of 3-methyl-1-butyn-3-ol (**1**, R_1 = CH_3, 20–50% of the volatile material), two further major components (20–30% each), and several minor components (less than 5% each) which were not investigated. Distillation, column chromatography, and preparative VPC led to the isolation of methyl 2-isopropyl-3-oxo-4-pentynoate (**5**) and methyl (*Z*)-2-ethyl-



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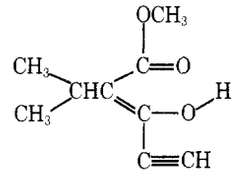


6

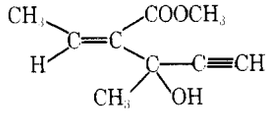
idene-3-hydroxy-3-methyl-4-pentynoate (**7**) besides the known[3] alcohol **1**.

The structure of **5** follows from spectroscopic evidence. The IR spectrum shows the presence of an acetylenic proton at 3305 cm^{-1}, a peak of medium intensity for a conjugated triple bond at 2095 cm^{-1}, and two carbonyl absorptions at 1745 and 1685 cm^{-1}. The ^1H NMR spectrum confirms the presence of an ester methyl group, of an acetylenic proton, and of an iso-

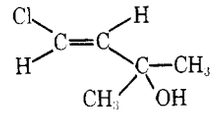
propyl group adjacent to a proton at δ 3.35 ppm which is slowly exchanged by added D_2O (H at C-2). In addition the spectrum displays peaks ascribed to the enol **6** which is present to the extent of ca. 8% in $CDCl_3$ or Me_2SO-d_6. The ^{13}C NMR spectrum and the UV spectrum are fully consistent with the proposed structure (see Experimental Section). The mass spectrum displays the molecular ion at *m/e* 168 and a base peak at *m/e* 126 due to a McLafferty rearrangement. Additional support for the β-keto ester function comes from a positive ferric chloride test. With the structure of β-keto ester **5** proven, it is now also clear why 2-methyl-4-hexanone (**4**, $R_1 = CH_3$) was found by Rhinesmith[1] on catalytic hydrogenation of the reaction product followed by decarboxylation of the resulting saturated β-keto ester with methanolic potassium hydroxide.

The IR spectrum of **7** shows a hydroxy group (3450 cm^{-1}, broad), a proton bonded to a triple bond (3310 cm^{-1}), and an unsaturated ester at 1720 cm^{-1}. The ^1H NMR spectrum confirms the presence of an ester methyl group, of a hydroxy and an acetylenic proton, of a methyl group at a quaternary carbon, and a methyl group coupled (J = 7 Hz) with a vinylic proton at δ 6.55 ppm. Additional evidence for the structure of **7** comes from the broad band and off-resonance decoupled ^{13}C NMR spectra which display the ester carbonyl carbon, two vinylic and two acetylenic carbon atoms, a fully substituted carbon bearing an oxygen function, and three methyl carbon atoms. The UV spectrum is consistent with the structure of an α-substituted crotonic ester. The mass spectrum shows a very weak molecular ion (*m/e* 168, 0.5%) and a prominent peak for loss of CH_3 which is also found with the acetylenic alcohol **1**. The *Z* configuration of the double bond follows from the ^1H NMR spectrum in the presence of Eu(fod)$_3$.[4] The europium complexes at the hydroxy group alone, and the large shift induced at the vinyl proton indicates a cis relationship between this proton and the carbinol function.

When the addition product of methylmagnesium iodide with methyl propiolate is hydrolyzed with ammonium chloride instead of ammonium sulfate, the product mixture is even more complex. Besides **1**, **5**, and **7**, (*E*)-1-chloro-3-methyl-



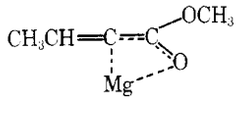
7



8

1-buten-3-ol (**8**, ca. 5% of the volatile products) was isolated and identified by spectroscopic methods and comparison with material obtained by reduction of 1-chloro-3-methyl-1-butyn-3-ol with lithium aluminum hydride.[5]

The formation of both compounds **5** and **7** can be explained by 1,4-addition of methylmagnesium iodide to methyl propiolate to yield the vinyl Grignard compound **9**, which then



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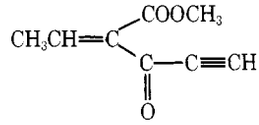

10

adds to the ester function of another molecule of methyl propiolate. The resulting unsaturated keto ester **10** reacts with excess methylmagnesium iodide either by a 1,2-addition to the keto carbonyl function to give alcohol **7**, or by a 1,4-addition to the ethylenic carbonyl function leading to β-keto ester **5**.[6]

Experimental Section

General. IR spectra were measured on a Perkin-Elmer 177 spectrometer. NMR spectra were obtained on a Bruker WH-90 FT spectrometer at 90 (^1H NMR) or 22.63 MHz (^{13}C NMR) using tetramethylsilane as an internal standard. UV spectra were recorded on a Beckman DK 2 spectrometer, and mass spectra on a AEI-MS 30 at 70 eV. VPC analyses and separations were carried out on a Perkin-Elmer 3920 chromatograph using glass columns packed with SE-52 or Carbowax 20M on Chromosorb DMCS. Combustion microanalyses were carried out by Mr. E. Thommen.

Grignard Reaction. A solution of 14.2 g (100 mmol) of freshly distilled methyl iodide in ethyl ether (40 mL) was added dropwise with stirring to 2.43 g (100 mmol) of magnesium under nitrogen. After refluxing for 30 min, the reaction mixture still contained some unreacted magnesium. It was cooled to −5 °C in an ice/salt mixture, and a solution of 1.68 g (20 mmol) of methyl propiolate (Fluka, freshly distilled) in ethyl ether (15 mL) added at such a rate that the temperature remained between −5 and 0 °C. The reaction mixture was stirred at 0 °C for an additional 15 min, then poured into a large excess of cooled, saturated aqueous ammonium sulfate. The mixture was extracted twice with ethyl ether, and the extractions were washed with aqueous sodium chloride, stabilized by the addition of a trace of hydroquinone, and dried over magnesium sulfate. The solution was analyzed by VPC, then concentrated on a vacuum rotary evaporator and distilled in a Kugelrohr at 120 °C (12 mm) to give 0.49 g (29%) of a yellowish oil. Redistillation led to the separation of **1** and low-boiling impurities. The remaining oil was chromatographed on silica gel with petroleum ether/ethyl ether. Fractions rich either in **5** or in **7** were obtained and purified by preparative VPC.

3-Methyl-1-butyn-3-ol (1)[3] was a colorless oil: bp 130 °C (Kugelrohr); IR (CCl_4) 3620 (OH), 3315 (≡CH), 2120 w (C≡C), 953, 882 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (s, 6 H, CH_3), 1.9 (s, 1 H, OH), 2.42 (s, 1 H, ≡CH); MS *m/e* 83 ($M^+ - 1$, 6.5%), 69 ($M^+ - CH_3$, 100).

Methyl 2-isopropyl-3-oxo-4-pentynoate (5) was a slightly yellow oil: bp 120 °C (12 mm) (Kugelrohr); IR (CCl_4) 3305 (≡CH), 2095 m (C≡C), 1745, 1685 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.01 (d, J = 7 Hz, 6 H, CH_3), 1.6 (m, 1 H, CH), 3.34 (s, 1 H, ≡CH), 3.35 (d, J = 8 Hz, 1 H, slowly exchangeable with D_2O in Me_2SO-d_6, H at C-2), 3.75 (s, 3 H, OCH_3), and peaks for the enol **6** (8 ± 2%) at δ 1.17 (d), 3.46 (s), 3.82 (s), 11.7 (in Me_2SO-d_6, OH); ^{13}C NMR ($CDCl_3$) δ 20.2 (q, CH_3), 20.4 (q, CH_3), 28.7 (d, CH), 52.4 (q, CH_3O), 67.8 (d, CH-2), 80.9 (d, ≡CH), 81.8 (s, ≡C–), 168.4 (s, COO), 181.9 (s, CO); MS *m/e* 168 (M^+, 4), 153 (11), 137 (33), 126 (100); UV (cyclohexane) 210 nm (log ϵ 3.58), 276 (3.06).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.11; H, 7.36.

Methyl (*Z*)-2-ethylidene-3-hydroxy-3-methyl-4-pentynoate (7) was a colorless oil: bp 120 °C (12 mm) (Kugelrohr); IR (CCl_4) 3610, 3450 b (OH), 3310 (≡CH), 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.71 (s, 3 H, CH_3), 1.94 (d, J = 7 Hz, 3 H, CH_3), 2.55 (s, 1 H, ≡CH), 3.85 (s, 3 H, OCH_3), 3.91 (s, 1 H, OH), 6.55 (q, 1 H, =CH). Induced shift by Eu(fod)$_3$[4] calculated from eight measurements in the range of 0.05–0.6 molar ratio, substrate 0.15 M in $CDCl_3$, gradient G (ppm) OH (29), CH_3CO (7.8), =CH (5.1), ≡CH (2.6), $=CCH_3$ (2.0), OCH_3 (1.5). ^{13}C NMR ($CDCl_3$) δ 15.4 (q, CH_3), 29.4 (q, CH_3), 51.6 (q, CH_3O), 68.8 (s, CO), 72.6 (d, ≡CH), 86.2 (s, ≡C). 133.5 (d, =CH), 136.6 (s, =C), 168.4 (s, COO); MS *m/e* 168 (M^+, 0.5), 153 (48), 121 (100); UV (cyclohexane) 214 nm (log ϵ 3.68).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.33; H, 7.32.

When the Grignard reaction mixture was hydrolyzed with aqueous ammonium chloride, **(*E*)-1-chloro-3-methyl-1-buten-3-ol (8)** was isolated by distillation and preparative VPC: colorless oil; bp 60 °C (12 mm) (Kugelrohr); IR (CCl_4) 3615, 3400 b (OH), 3085 (=CH), 1624 (C=C), 932 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 6 H, CH_3), 1.50 (s, 1 H, OH), 6.05 and 6.27 (AB, J = 13.5 Hz, 1 H each, =CH); MS *m/e* 107 ($M^+ - CH_3$, 31), 105 ($M^+ - CH_3$, 100), 85 ($M^+ - Cl$, 65).

Independent Synthesis of 8. A suspension of 0.21 g (5.5 mmol) of lithium aluminum hydride in ethyl ether (20 mL) was added dropwise with stirring to 0.62 g (5.2 mmol) of 1-chloro-3-methyl-1-butyn-3-ol[5] in ethyl ether (20 mL) at 0 °C under nitrogen. After 3 h at 0 °C, 1 mL of 1 N NaOH was added drop by drop, the resulting crystalline precipitate filtered off, and the filtrate distilled to give 0.53 g (84%) of a colorless oil, bp 92–96 °C (100 mm), identical (IR, NMR, MS, VPC) with the material obtained above.

Anal. Calcd for C_5H_9OCl: C, 49.80; H, 7.52; Cl, 29.40. Found: C, 49.89; H, 7.72; Cl, 29.06.

Acknowledgment is made to Professor P. W. Schiess, who suggested the problem, and Dr. U. Séquin for helpful advice. We thank also the CIBA-GEIGY AG for financial support.

Registry No.—**1** ($R_1 = CH_3$), 115-19-5; **5**, 62493-29-2; **6**, 62493-28-1; **7**, 62493-30-5; **8**, 62493-31-6; methyl propiolate, 922-67-8; 1-

chloro-3-methyl-1-butyn-3-ol, 29552-15-6; methylmagnesium iodide, 917-64-6.

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(3) D. D. Coffman, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 320.
(4) Eu(fod)$_3$ = tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadionato)-europium(III). For a general account on lanthanide shift reagents see A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
(5) M. Julia and J. M. Surzur, *Bull. Soc. Chim. Fr.*, 1615 (1956).
(6) The mode of formation of **8** is not clear at the moment. A blank reaction of alcohol **1** with excess methylmagnesium iodide gave no trace (<0.1%) of **8** upon workup with ammonium chloride.

Lithiation of 4,4-Dimethyl-2-(2-thienyl)-2-oxazoline

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Numerous aromatic substituents with ortho-directing metalation abilities have been reported and their synthetic potential has been discussed.[1] The knowledge of the relative directing effect of these groups has become increasingly important for synthetic planning. For the benzene ring, a relative order of ortho-directing strength for some of these substituents has been recently established.[2] In heteroaromatic compounds, the ortho-directing group competes with the heteroatom in the aromatic ring for the site of metalation. Slocum and co-workers have recently reported[3] that the lithiation of thiophene substituted at the 2 position with strong ortho directors, such as carboxamides, sulfonamides, and dimethylaminomethyl groups, leads to metalation at the 5 position (α-lithiation) rather than the 3 position (ortho lithiation) of the thiophene nucleous. Kauffman and co-workers, on the other hand, observed[4] that the lithiation of 2-(2-pyridyl)-thiophene leads to mixtures of 3- and 5-lithiothiophene derivatives and that the product ratio is greatly affected by the solvent of the lithiation reaction. We wish now to report that the metalation of 2-(2-thienyl)-2-oxazoline **1** in ether proceeds predominantly ortho to the oxazoline group.

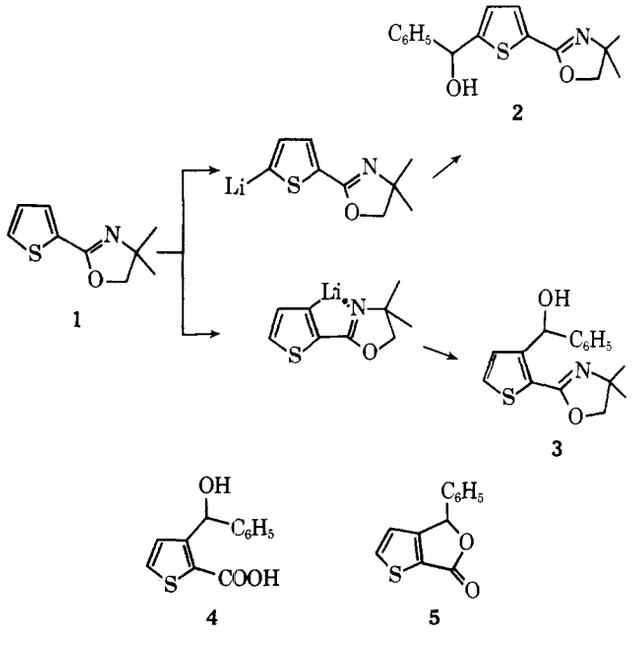

Table I

Lithiating reagent	Solvent	Temp, °C	Metalation time, h	Yield, %[b] Isomer 2	Isomer 3
n-BuLi	THF	−70	1	55	36
sec-BuLi	Ether	−70	1	2.3	81.3
n-BuLi	Ether	−70–0	0.75[a]	4.1	91

[a] 0.25 h at −70 °C and 0.5 h at 0 °C. [b] Based on the starting oxazoline **1**. Recovered oxazoline **1** constitutes the balance of the material.

This investigation of the metalation of **1** was prompted by our need for an efficient synthesis of 3-substituted thiophene-2-carboxylic acids and was based on the well-known ortho-directing ability of the oxazoline[5] group and the easy accessibility of **1**.[6] Lithiation of **1** with *n*-BuLi in ether or THF followed by condensation with benzaldehyde gave mixtures of products **2** and **3**, with the desired isomer **3** being clearly favored in ether. The metalation results are summarized in Table I. The structural assignments of the two isomers were based on their NMR spectra and were also verified by hydrolysis[6] of **3** to the acid **4** and conversion to the lactone **5**.

In synopsis, the lithiation of 2-(2-thienyl)-2-oxazoline **1** provides an efficient route to 2,3-disubstituted thiophenes. Our results, together with those of Kauffman[4] and Slocum,[3] seem to establish a relative order of ortho-directing substituents in thiophene as follows: oxazoline > pyridyl > sulfonimides, carboxamides, and dimethylaminomethyl.

Experimental Section

4,4-Dimethyl-2-(2-thienyl)-2-oxazoline (1). To a solution of 2-thiophenecarboxyl chloride (100 g, 0.68 mol) in methylene chloride (200 mL) a solution of 2-amino-2-methyl-1-propanol (121.6 g, 1.36 mol) in methylene chloride (500 mL) was added dropwise while maintaining the temperature below 20 °C. The mixture was stirred at room temperature for 2 h and washed with water, and the organic layer was dried over $MgSO_4$ and evaporated. The residue was suspended in benzene (600 mL) and thionyl chloride (270.7 g, 2.28 mol) was added dropwise with stirring while maintaining the temperature below 30 °C. The stirring continued overnight, the benzene was evaporated at aspirator pressure, the residue was dissolved in water, and then the solution was basified with 1 N aqueous NaOH and extracted twice with ether. The ether extracts were dried over $MgSO_4$ and evaporated, and the residue was distilled to give 90 g of oxazoline **1**: bp 71–73 °C (0.1 mm Hg); NMR ($CDCl_3$) δ 7.63 (d of d, 1 H, J = 5 and 2 Hz, 5-thienyl-H), 7.44 (d of d, 1 H, J = 6 and 3 Hz, 3-thienyl-H), 7.05 (d of d, 1 H, J = 5 and 6 Hz, 4-thienyl-H), 4.06 (s, 2 H, $-OCH_2$), 1.35 (s, 6 H, 2× CH_3). Anal. Calcd for $C_9H_{11}NOS$: C, 59.64; H, 6.12; N, 7.73. Found: C, 59.35; H, 6.29; N, 7.92.

Lithiation Procedure. To a solution of 4,4-dimethyl-2-(2-thienyl)-2-oxazoline (**1**) in ether or THF (5 mmol of oxazoline in 20 mL of solvent) the lithiating reagent was added dropwise at −70 °C with stirring under nitrogen. The reaction mixture was stirred at the designated temperature for the designated time, the benzaldehyde (5 mmol) was added, and the mixture was allowed to warm up to room temperature. It was poured into water and extracted with ether. The ether extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was subjected to preparative thin-layer chromatography (SiO_2, on CH_2Cl_2:EtOAc, 9:1) to give the less polar 2-(3-hydroxyphenylmethyl-2-thienyl)-4,4-dimethyl-2-oxazoline **3** [oil; R_f 0.68; NMR ($CDCl_3$) δ 6.72 (d, 1 H, J = 5.3 Hz, 4-thienyl-H), 6.07 (s, 1 H, PhCH–), 4.01 (s, 2 H, OCH_2), 1.33 (s, 3 H, CH_3), 1.2 (s, 3 H, CH_3). Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.51; H, 6.2; N, 5.06] and the polar isomer **2** [mp 121–124 °C; R_f 0.11; NMR ($CDCl_3$) δ 6.84 (d, 1 H, J = 3.5 Hz, 4-thienyl-H), 6 (s, 1 H, PhCH), 4.02 (s, 2 H, OCH_2), 1.27 (s, 6 H, 2× CH_3). Anal. Found: C, 66.05; H, 6.01; N, 5.03].

4-Phenylthieno[2,3-*c*]furan-6(*4H*)-one (5). A mixture of the oxazoline **3** (344 mg, 0.0012 mol) and 3 N aqueous hydrochloric acid was refluxed for 10 min and evaporated under aspirator pressure. The residue was stirred with 40% aqueous NaOH (3.6 mL) at room temperature for 10 min, methanol (3.6 mL) was added, and the mixture was refluxed for 30 min. It was poured into water, acidified with 6 N