taken on a Perkin-Elmer Model 337 infrared spectrophotometer and are reported in reciprocal centimeters with polystyrene as the reference standard. High-resolution mass spectra were recorded on a Kratos MS-50 mass spectrometer using a Kratos DS-55 data system. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

17β-[(*tert*-Butyldimethylsilyl)oxy]-5,5-(ethylenedioxy)-2,5-seco-3,4-dinorandrostan-2-yl Thiobenzoate (12). To a stirred solution of 8.26 g (40 mmol) of triphenylphosphine in 40 mL of dry THF under argon at 0 °C was added 0.08 g (40 mmol) of diisopropyl azodicarboxylate in 8 mL of THF. A solid formed after 30 min of stirring, and a solution of 8.44 g (20 mmol) of 17β-[(*tert*-butyldimethylsilyl)oxy]-5,5-ethylenedioxy-2-hydroxy-2,5-seco-3,4-dinorandrostane (**3b**) and 4.8 mL of thiobenzoic acid in 40 mL of dry THF was added over a 5-min period. The resulting solution was stirred at 0 °C for 90 min and 1 h at 25 °C. The reaction mixture was then poured into 300 mL of CH_2Cl_2, washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated to give 20 g of an oil that was filtered through a column of 500 mL of silica gel with 5% EtOAc/hexane and purified by preparative HPLC using 2% EtOAc/hexane. The pure fractions were combined, concentrated, and recrystallized from EtOH to give 6.2 g (11.1 mmol, 56%)[6] of pure thio ester **12**: mp 110–111 °C (EtOH); IR (KBr) 1660 cm^{-1}; NMR δ 0.08 (s, 6 H), 0.70 (s, 3 H), 0.85 (s, 9 H), 1.00 (s, 3 H), 3.25 (m, 2 H, SCH_2), 3.51 (t, 1 H, J = 7 Hz), 3.95 (m, 4 H), 7.40 (m, 3 H), 7.85 (m, 2 H).

Anal. Calcd for $C_{32}H_{50}O_4SSi$: C, 68.77; H, 9.02; S, 5.74. Found: C, 68.68; H, 9.10; S, 6.05.

17β-[(*tert*-Butyldimethylsilyl)oxy]-5,5-(ethylenedioxy)-2,5-seco-3,4-dinorandrostan-2-yl Disulfide (13). To a stirred mixture of 4.2 g (7.5 mmol) of thio ester **12** in 150 mL of 95% EtOH at 25 °C open to the air was added 10 mL of 1 N LiOH. The mixture turned pale yellow, and a precipitate formed as stirring was continued for 72 h. The mixture was gradually diluted with 50 mL of water, chilled to 0 °C, and filtered. The filtrate was washed with water and vacuum-dried to yield 3.2 g (3.5 mmol, 94% yield) of analytically pure crystals: mp 150–151 °C; NMR δ 0.09 (s, 6 H), 0.70 (s, 3 H), 0.85 (s, 9 H), 0.95 (s, 3 H), 2.75 (m, 2 H), 3.50 (t, 1 H, J = 7 Hz), 3.85 (m, 4 H).

Anal. Calcd for $C_{50}H_{90}O_6S_2Si_2$: C, 66.17; H, 10.06; S, 7.07. Found: C, 65.83; H, 9.77; S, 7.16.

17β-Hydroxy-3-thiaandrost-4-ene (14). To a stirred mixture of 1.43 g (4.0 mmol) of methyltriphenylphosphonium bromide in 50 mL of dry ether under argon at −78 °C was added 2.6 mL (4.0 mmol) of 1.55 M *n*-butyl lithium. The mixture was allowed to warm to 0 °C and stirred for 30 min. A solution of 906 mg (1.0 mmol) to disulfide **13** in 15 mL of dry ether was added over a 2-min period. After stirring at 0 °C for 30 min, 4 mL 1 N HCl was added and the ether was evaporated in vacuo. The residue was diluted with 20 mL of H_2O and triturated with three 20-mL portions of hexane to remove any thiol byproducts. These byproducts were isolated, dissolved in ethyl alcohol, and treated with excess LiOH in air to yield 288 mg (0.31 mmol) of recovered disulfide **13**.

The aqueous mixture was made homogeneous with ethyl alcohol and acidified to pH 1 with 6 N HCl and then stirred at 25 °C for 96 h. The solution was lyophilized. The residue was transferred to a 60-mL pear-shaped flask with absolute EtOH, evaporated to dryness, and heated at 80 °C under high vacuum. The resulting solid was dissolved in 6 mL of dry Me_2SO and treated with 800 mg of potassium *tert*-butoxide at 80 °C under argon for 3 h. The cooled solution was poured into 50 mL of water and extracted with three 50-mL portions of CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. Chromatography of the residue on 20 mL of silica gel with 20% EtOAc/hexane gave 114 mg (0.39 mmol, 39% yield) of a white solid: mp 135–136 °C; NMR δ 0.07 (s, 6 H), 0.75 (s, 3 H), 1.00 (s, 3 H), 2.5–3.0 (m, 2 H), 3.60 (t, 3 H, J = 7 Hz) 5.60 (br, 1 H).

Anal. Calcd for $C_{18}H_{28}OS$: C, 73.92; H, 9.65; S, 10.96. Found: C, 74.11; H, 9.67; S, 10.62.

17β-Hydroxy-3-sulfinylandrost-4-ene (15). To a solution of 65 mg (0.22 mmol) of 17β-hydroxy-3-thiaandrost-4-ene (**14**) in 2 mL of dioxane was added a solution of 53.5 mg (0.25 mmol) of sodium metaperiodate in 0.5 mL of H_2O. The resulting solution was stirred at 25 °C for 18 h. The resulting mixture was diluted with 10 mL of 5% EtOH/EtOAc and filtered. The filtrate was concentrated to dryness, and the residue was taken up in 10 mL of hot 5% EtOH/EtOAc, filtered, and concentrated to yield 70 mg of nonuniform crystals. High-vacuum heating caused discoloration. TLC showed two polar products in ~2:1 ratio with R_f's of 0.17 and 0.22 (20% EtOH/EtOAc), respectively: IR (KBr) 3400, 1000 cm^{-1}; NMR δ 0.80 (s, 3 H), 1.10 (s, 3 H), 3.65 (t, 1 H, J = 7 Hz), 5.95 (m, $^1/_3$H), 6.20 (br s, $^2/_3$H); mass spectrum (70 ev), M^+ calcd for $C_{18}H_{28}O_2S$ 308.1810, found 308.1795 ± 0.0024, base peak at m/e 291 (M − 17).

Acknowledgment. Appreciation is extended to Louis Shadoff of Midland Analytical Laboratories for performiong high-resolution mass spectrometry.

Registry No. **1** (isomer 1), 87116-07-2; **1** (isomer 2), 87116-08-3; **3b**, 87116-09-4; **4**, 58-22-0; **8**, 51154-10-0; **9**, 17541-44-5; **10**, 87116-10-7; **10** ($SiMe_2Bu$-*t* ester), 87116-11-8; **11**, 87116-12-9; **12**, 87136-10-5; **13**, 87136-11-6; **14**, 87116-13-0; $(Ph)_3P{=}CH_2$, 3487-44-3.

Simplified Method for O-Alkylation of N-Protected Tyrosines

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Modification of the phenolic hydroxyl group of tyrosine has proven to be a useful approach in the design of biologically active peptides.[1] This strategy has been extensively applied, for example, by Manning and Sawyer[1c,d] in the synthesis of a number of antidiuretic antagonists of vasopressin. Despite the conceptual simplicity of the phenolic alkylation of tyrosine by the Williamson synthesis, to date no direct method exists that produces aliphatic ethers of tyrosine or N-protected tyrosine in a single step by using commercially available inexpensive reagents and solvents.

Previously, Solar and Schumaker[2] prepared the C-4 to C-10 primary alkyl ethers of tyrosine, but their method was not useful for preparing secondary ethers. Additionally, these authors did not comment on the optical purity of their tyrosine ethers, despite the stringent reaction conditions (10% NaOH in Me_2SO, 80–115 °C) that could lead to partial racemization.

A recently published method by Kolodziejczyk and Manning has provided at least a partial solution to the problem of finding a direct alkylation method.[3] Their described method as applied to tyrosine carbamates, however, still lacks the elements of simplicity. Thus, the required preparation of carcinogenic alkylating agents, coupled with the use of benzene and crown ether, is undesirable in an industrial scale of operation.

We now report a safe, inexpensive, and direct method for the preparation of a wide range of N-protected tyrosine alkyl ethers (Scheme I). Our procedure is based on a chemoselective monoalkylation of tyrosine disodium salt

(1) (a) Law, H. D.; duVigneaud, V. *J. Am. Chem. Soc.* **1960**, *82*, 4579. (b) Zhuze, A. L.; Jost, K.; Kasafirek, E.; Rudinger, J. *Collect. Czech. Chem. Commun.* 1964, *29*, 2648. (c) Sawyer, W. H.; Pang, P. K. T.; Seto, J.; McEnroe, M.; Lammek, B.; Manning, M. *Science (Washington, D.C.)* **1981**, *212*, 49. (d) Manning, M.; Olma, A.; Klis, W. A.; Kolodziejczyk, A. M. *J. Med. Chem.* **1982**, *25*, 45.

(2) Solar, S. L.; Schumaker, R. *J. Org. Chem.* **1966**, *31*, 1996.

(3) Kolodziejczyk, A. M.; Manning, M. *J. Org. Chem.* **1981**, *46*, 1944.

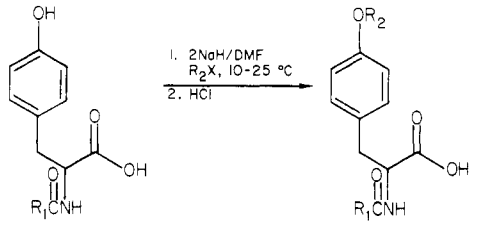
0022-3263/83/1948-4127$01.50/0

Table I. Summary of N-Protected Tyrosine Alkylations

run	tyrosine derivative	alkylating agent	reaction time, h (temp, °C)	yield, % (corrected)	mp, °C	$[\alpha]^{25}_D$;[n] deg
1	1 (L isomer)	CH_3Br	5.5 (10)	73[a]	89-91 (92-94)[k]	+30.6 (+31.0)[j]
2	1 (L isomer)	CH_3I	3 (10)	77[a]	92-93	+33.2
3	1 (L isomer)	C_2H_5Br	4 (10)	79[a]	82-84 (90-92)[k]	+31.6 (+30.3)[j]
4	1 (D isomer)	C_2H_5Br	4.5 (10)	55[a]	82-84 (90-92)[k]	−31.6 (−30.4)[m]
5	1 (L isomer)	C_2H_5I	3 (10)	35[b]	82-84	+31.4
6	1 (L isomer)	n-C_3H_7Br	19 (10-25)	67[a]	76-78 (84-86)[k]	+33.5 (+31.5)[k]
7	1 (L isomer)	n-C_3H_7I	19 (10-25)	(oil)[b]		
8	1 (L isomer)	sec-C_4H_9Br	19 (10-25)	82[c,d]	116-117[e]	+37.9[e]
9	1 (L isomer)	sec-C_4H_9I	19 (10-25)	38[c,d]	115-116[e]	+40.5[e]
10	1 (L isomer)	c-C_5H_9Br[g]	19 (10-25)	63[d,f]	116-117 (148-149)[e]	+27.3 (+35.5)[e]
11	2 (L isomer)	C_2H_5Br	3.5 (10)	74	77-78 (79-81)[k]	−34.4 (DMF)[l] (−35.1, DMF)[k]
12	2 (L isomer)	i-C_3H_7Br	19 (10-25)	68[d,h]	78-80	+16.2
13	2 (L isomer)	c-C_5H_9Br	19 (10-25)	53[i]	176-177[e]	+8.1[e]

[a] Crude reaction contained 4-8% 1 via HPLC. [b] Resisted crystallization; crude appeared chromatographically similar to alkyl bromide reaction product. [c] Crude reaction, 30% 1 via HPLC. [d] Following flash chromatography[6] on silica gel. [e] As the dicyclohexylamine salt. [f] Crude reaction, 20% 1 via HPLC. [g] Cyclohexyl bromide failed to react. [h] Crude reaction, 14% 2 via HPLC. [i] Crude reaction, 47% 2 via HPLC. [j] Bachem sample $[\alpha]^{25}_D$ (c 1, ethanol). [k] Reference 3. [l] $[\alpha]^{25}_D$ +14.2° (c 1, ethanol). [m] Prepared by method of Kolodziejczyk and Manning, ref 3. [n] c 1, ethanol; reference values in parentheses.

Scheme I[a]



1, $R_1 = (CH_3)_3CO$
2, $R_1 = C_6H_5CH_2O$

[a] R_2 = alkyl, cycloalkyl (Table I).

by alkyl halides in DMF.[4] Commercially available *t*-Boc- and Cbz-protected tyrosines are the starting materials, and methyl, ethyl, *n*-propyl, isopropyl, cyclopentyl, and *sec*-butyl halides function as the alkylating agents. It is noteworthy that in the cases where compared, the alkyl bromides gave consistently purer and more easily crystallizable products than the corresponding alkyl iodides.

Typically, the N-protected tyrosine **1** or **2**[5] is dissolved in DMF and cooled to 10 °C. After addition of 2.3 equiv of sodium hydride,[7] the reaction is stirred at that temperature for 1 h and then the halide is added in a single portion. The reaction is completed by stirring at 10/25 °C (see Table I). If the product was not crystalline, it was converted to the dicyclohexylamine salt for characterization.

The procedure gives excellent discrimination between the alkylation of phenolate or carboxylate anion. Only in the reaction of **1** with *sec*-butyl halides was competing ester formation discernable (HPLC examination of the crude reaction product).

The tyrosine ethers prepared by this alkylation method were >99% optically pure. This was demonstrated by comparison of their optical rotation with commercial samples; additionally, the satisfactory optical purity of one of our products prepared by our standard procedure was verified by conversion to a diasteromeric dipeptide and HPLC analysis of the product by the method of Takaya.[8]

Experimental Section

Melting points were uncorrected. Optical rotations were run as a 1% solution in 95% ethanol on a Perkin-Elmer 241 MC polarimeter at 25 ± 1 °C in a 1-dm cell. All reaction products gave satisfactory C, H, and N microanalyses and mass spectra. The reactions were monitored by HPLC analysis on a μBondapak-C18, 3.9 × 30 mm column, using a Perkin-Elmer Series 3B instrument and a Perkin-Elmer Model LC-75 detector operating at λ 254 nm. Mobile phase: A, 1% acetic acid in acetonitrile; **B**, 1% acetic acid (gradient 40–80% A over 20 min).

Typical Alkylation Procedure. *t*-Boc-L-tyrosine (5 g, 17.8 mmol) was dissolved in dry DMF (75 mL), the solution was cooled to 10 °C, and a sodium hydride suspension (60% in mineral oil, 1.65 g, 41 mmol) was added all at once. After stirring for 1 h at 10 °C, methyl iodide (2.53 g, 17.8 mmol) was added. After the reaction mixture had stirred 3 h at 10 °C, ice water (150 mL) and ethyl acetate (400 mL) were added. The aqueous phase was separated, extracted twice with ethyl acetate (75 mL), and acidified with 6 N HCl with cooling. The product was extracted into ethyl acetate (3 × 75 mL), washed with water, and dried ($MgSO_4$). The crude white solid obtained on evaporation (4.33 g) was recrystallized from toluene–hexane: 3.92 g, (74%) mp 92–93 °C (13.3 mm).

In several cases our alkylation products (Table I) had melting points 6–8° lower than those reported.[3] However, the melting points of alkylation products that we prepared by the reported method (ref 3) were very much in line with our own reported values (see Table I).

Optical Purity Determination of *t*-Boc-L-tyrosine Ethyl Ether: Conversion to *t*-Boc-L-Tyr(Et)-L-Phe-OMe.[8] A solution of L-phenylalanine methyl ester (Aldrich, 0.448 g, 2.5 mmol) liberated with potassium carbonate from its hydrochloride, *t*-Boc-L-tyrosine ethyl ether (run 3 above; 0.772 g, 2.5 mmol), and 1-hydroxybenzotriazole hydrate (0.34 g, 2.52 mmol) in DMF (5 mL) was cooled to −5 °C, treated with dicyclohexylcarbodiimide (0.51 g, 2.48 mmol), and stirred overnight (−5 °C). The reaction was allowed to warm to room temperature for 1.5 h, and the dicyclohexylurea was removed by filtration and washed with ethyl acetate. The filtrate was diluted with water and ethyl acetate, and the layers were separated. The organic layer was washed with water and saturated sodium chloride and dried ($MgSO_4$).

(4) *N*-(*tert*-butoxycarbonyl)-*O*-benzyl-L-serine has been prepared by a similar procedure: Sugano, H.; Miyoshi, M. *J. Org. Chem.* **1976**, *41*, 2352.

(5) D- and L-*t*-Boc-Tyr and L-Cbz-Tyr were purchased from Chemical Dynamics Corp.

(6) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(7) Sodium hydride/DMF have been observed to self-heat as low as 50 °C via calorimetry; a thermal runaway reaction was recently reported from our laboratory. Buckley, J.; Webb, R. L.; Laird, T.; Ward, R. J. *Chem. Eng. News* **1982**, *60*, 5.

(8) Takaya, T.; Kishida, Y.; Sakakibara, S. *J. Chromatog.* **1981**, *215*, 279.

Evaporation gave a residue, which solidified on standing overnight. HPLC analysis of the crude dipeptide (μPorasil, 3.9 × 30 mm) gave a single peak, t_R 5.76 min (85:15 hexane:2-propanol). The D,L-dipeptide prepared analagously had a retention of 6.41 min. In this manner we observed less than 0.2% of the D,L-dipeptide in our sample, thus reflecting >99.8% optical purity for our O-alkylated tyrosine.

Acknowledgment. We are grateful to Edith Reich for microanalyses and optical rotations; D. Staiger, G. Zuber, G. D. Roberts and L. B. Killmer provided NMR and mass spectra. We express appreciation to Monica M. Holmes for her technical assistance.

Registry No. L-1, 3978-80-1; D-1, 70642-86-3; L-2, 1164-16-5; CH_3Br, 74-83-9; CH_3I, 74-88-4; C_2H_5Br, 74-96-4; C_2H_5I, 75-03-6; n-C_3H_7Br, 106-94-5; n-C_3H_7I, 107-08-4; sec-C_4H_9Br, 78-76-2; sec-C_4H_9I, 513-48-4; c-C_5H_9Br, 137-43-9; i-C_3H_7Br, 75-26-3; t-Boc-L-Tyr(OEt)-L-Phe-OMe, 87190-95-2; t-Boc-D-Tyr(OEt)-L-Phe-OMe, 87190-96-3; t-Boc-L-tyrosine methyl ether, 53267-93-9; t-Boc-L-tyrosine ethyl ether, 76757-91-0; t-Boc-D-tyrosine ethyl ether, 76757-92-1; t-Boc-L-tyrosine propyl ether, 76757-93-2; t-Boc-L-tyrosine sec-butyl ether dicyclohexylamine salt, 87190-91-8; t-Boc-L-tyrosine cyclopentyl ether, 82152-22-5; Cbz-L-tyrosine ethyl ether, 66147-90-8; Cbz-L-tyrosine isopropyl ether, 87190-92-9; Cbz-L-tyrosine cyclopentyl ether dicyclohexylamine salt, 87190-94-1; cyclohexyl bromide, 108-85-0; L-phenylalanine methyl ester, 2577-90-4.

Addition of Piperidine to Some 2-Alkylbenzo[*b*]thiophene 1,1-Dioxides

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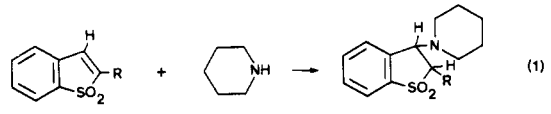
Within the framework of our systematic studies of the chemistry[1a] and photochemistry[1b] of the benzo[*b*]thiophene system, it was of interest to prepare 3-piperidino-2-methyl-2,3-dihydrobenzo[*b*]thiophene. The addition of piperidine to 2-methylbenzo[*b*]thiophene 1,1-dioxide followed by the reduction of the adduct with lithium aluminum hydride[2] appeared to be the appropriate synthetic sequence. Benzo[*b*]thiophene 1,1-dioxide (**1a**),[3] its 2-bromo derivative **1b**,[4] and the 2-phenyl derivative **1c**[5] undergo addition reactions in a manner comparable to other α,β-unsaturated sulfones. In all these cases, the formation of a carbon–nitrogen bond takes place at the 3-position in the benzo[*b*]thiophene ring (eq 1).



(1)

1a, R = H; **1b**, R = Br; **1c**, R = C_6H_5

2a; **2b**; **2c**

(1) (a) Grandclaudon, P.; Lablache-Combier, A. *J. Org. Chem.* **1978**, *43*, 4379. (b) Grandclaudon, P.; Lablache-Combier, A. *J. Chem. Soc. D* **1971**, 892. Grandclaudon, P.; Lablache-Combier, A.; Párkányi, C. *Tetrahedron* **1973**, *29*, 651. Lablache-Combier, A.; Lerner, D.; Pollet, A. *J. Chem. Res. Synop.* **1978**, 38; *J. Chem. Res., Miniprint* **1978**, 281–286.

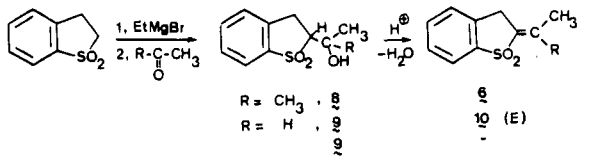
(2) Van Zyl, G.; de Jongh, D. C.; Heasley, V. L.; Van Dyke, J. W. *J. Org. Chem.* **1961**, *26*, 4946.

(3) Bordwell, F. G.; McKellin, W. H. *J. Am. Chem. Soc.* **1950**, *72*, 1985.

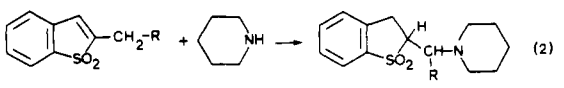
(4) Bordwell, F. G.; Lampert, B. B.; MeKellin, W. H. *J. Am. Chem. Soc.* **1949**, *71*, 1702.

(5) Centre d'Etudes pour l'Industrie Pharmaceutique, Ger. Offen. 1973, 2341894; *Chem. Abstr.* **1974**, *80*, 146007*f*.

Scheme I



However, reaction of the 2-alkylbenzo[*b*]thiophene 1,1-dioxides **1d** or **1e** with piperidine resulted in the formation of the unexpected adducts **3** and **4**, respectively, in which the amino group is bonded to the α-carbon atom of the side chain (eq 2). The addition reaction is slow, but the conversion of the starting sulfone is nearly quantitative within 100 h.[6]



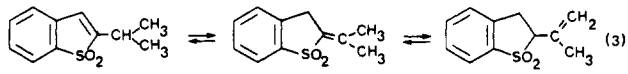
(2)

1d, R = H; **1e**, R = CH_3

3; **4**

Two adjacent centers of asymmetry are present in the compound **4**, resulting in erythro and threo diastereoisomers. The VPC and TLC analyses and ^1H and ^{13}C NMR spectra confirmed the formation of only one diastereoisomer but do not allow an unequivocal assignment of configuration. Compound **4** was subsequently identified as the threo diastereoisomer by single-crystal X-ray analysis.[7]

Treatment of 2-isopropylbenzo[*b*]thiophene 1,1-dioxide (**1f**) with piperidine or triethylamine gave a mixture of isomeric olefins in which the major product was the exocyclic olefin **6** (eq 3). Attempted isomerization of **1d** and **1e** in refluxing triethylamine resulted in a quantitative recovery of the starting material even after 2 weeks.



(3)

1f; **6**; **7**

We suggest that a rapid base-catalyzed isomerization of the sulfones **1d** and **1e** precedes the slow addition of the amine to the most reactive exocyclic olefins. The failure of the hindered **6** to add piperidine is consistent with the results of Stirling et al.[8] who have clearly shown the effect of the substitution in decreasing the reactivity of the double-bond toward amines. Because it cannot be obtained by isomerization, it was of interest to prepare the exocyclic olefin **10** by an alternate route. This was accomplished by the sequence depicted in Scheme I.

The metalation of 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide has been achieved with ethylmagnesium bromide[3] or n-butyllithium[9] with the same results. Condensation with acetaldehyde gave a 50:50 mixture of the threo[10] and erythro β-hydroxy sulfones **9**. Compound **8** was readily converted into **6** in a high yield by acid-catalyzed dehydration. The differences in the behavior of the threo and erythro β-hydroxy sulfones observed by Truce and Klinger[9] were also found in the case of **9**. The erythro isomer was converted into **10**, but the threo isomer was recovered

(6) Addition of cyclohexylamine is much slower[13] but leads to similar adducts.

(7) Abraham, F.; Trehoux, J.; Grandclaudon, P. *Acta Crystallogr., Sect C* **1983**, *39*, 483.

(8) McDowell, S. T.; Stirling, C. J. M. *J. Chem. Soc. B* **1967**, 351.

(9) Truce, W. E.; Klinger, T. C. *J. Org. Chem.* **1970**, *35*, 1834.

(10) The threo diastereoisomer of **9** was identified by single-crystal X-ray analysis. Trehoux, J.; Abraham, F.; Grandclaudon, P. *Acta Crystallogr., Sect C*, in press.

0022-3263/83/1948-4129$01.50/0