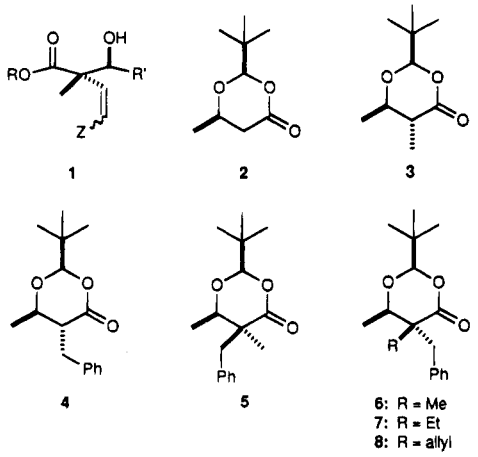
Stereocontrolled Formation of Quaternary Carbon Centers by Conjugate Addition of Lithium Enolates of Dioxanones to β-Bromoacrylates and β-Bromovinyl Sulfones: Dependence of Stereoselectivity on Alkene Geometry

Milan Bruncko and David Crich*

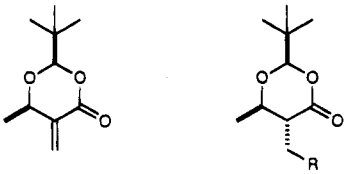
University of Illinois at Chicago, Department of Chemistry(M/C111), 845 West Taylor Street, Chicago, Illinois 60607-7061

Received August 2, 1994

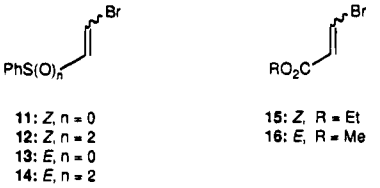
The efficient, stereocontrolled synthesis of quaternary carbon centers is a perennial problem in organic synthesis.[1] In the context of an ongoing natural product total synthesis we required an efficient means of formation of the system **1** in which Z is an electron withdrawing group, preferably the phenylsulfonyl group, and the olefin is either *cis* or *trans*. In this paper we report that such a system may be prepared in high yield and excellent diastereoselectivity by a conjugate addition/elimination process involving treatment of lithium enolates of 1,3-dioxan-4-ones with β-bromoacrylates and β-bromovinyl sulfones. We also report that the diastereoselectivity of the reaction is a function of the olefin geometry.



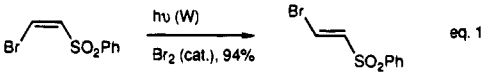
Seebach and co-workers have extensively studied alkylation reactions of **2**, which is readily derived from β-hydroxybutanoic acid and pivalaldehyde. Deprotonation with LDA followed by addition of alkyl halides results in clean alkylation with good stereocontrol anti to the C-6 methyl group as in **3** and **4**.[2] Unfortunately, early attempts at further alkylation of **3**, following deprotonation with LDA, with benzyl bromide were unsuccesful. However, it was found that **4** could be cleanly methylated by sequential treatment with LDA and methyl iodide giving a product that was initially assigned[2] structure **5** but which was later revised to **6**.[3] Subsequently, it was found that use of the Schwesinger PN base[4] in place of LDA enabled benzylation of **3** with the formation of **6**, opening the way to a potentially general route to quaternary carbon centers.[3b] Intriguingly, opposite face selectivity was observed in the alkylations of **3** and **4**. The possibility that this reversal of selectivity was due to the change in base from LDA to the PN base was ruled out when alkylation of **4** using the PN base and ethyl iodide or allyl bromide gave **7** and **8** with good diastereoselectivity. Eventually, it was concluded that the opposite face selectivity of enolates derived from **3** and **4** was a function of the benzyl group in the latter folding under and so shielding the bottom face.[3b,5] Cuprate and free radical additions to **9** leading preferentially to **10** are similarly rationalized.[4,6] Michael reactions of enolates of **3** have not been reported but it occured to us that if the enolates were sufficiently reactive then addition to β-bromoacrylates and to β-bromovinyl sulfones followed by elimination of bromide would provide an ideal entry to the targeted functionality (**1**).



The *Z*-bromovinyl sulfone **12** was prepared by the literature procedure, involving bromination and dehydrobromination of phenyl vinyl sulfide to give **11**, followed by peracid oxidation to the sulfone.[7] The *E*-bromovinyl



sulfone **14** had previously been prepared in low yield by separation of the *E*-sulfide **13** from **11**, in which it is a minor contaminent, by distillation followed by peracid oxidation.[7] We found it much more expedient to subject **12** to white light photolysis in the presence of a catalytic quantity of bromine which resulted in the formation of **14** (eq 1) in high yield. The *Z*- and *E*-bromoacrylates **15** and **16** were prepared by literature procedures.[8]



Deprotonation of (±)-**3** with LHMDS[9] in THF at −78 °C followed by addition of **14** resulted in a clean reaction and isolation of the Michael adduct **17** in 65% yield with a greater than 20:1 ratio of diastereomers. Conversely, reaction of the Li enolate of **3** under identical conditions

(1) See: (a) Martin, S. F. *Tetrahedron* **1980**, *36*, 419. (b) Fuji, K. *Chem. Rev.* **1994**, *94*, 2037. (c) Barta, N. S.; Brode, A.; Stille, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 6201 and references therein.

(2) Zimmermann, J.; Seebach, D. *Helv. Chim. Acta* **1988**, *71*, 1143.

(3) (a) Pietzonka, T.; Seebach, D. *Chem. Ber.* **1991**, *124*, 1837. (b) Scherovsky, G.; Sefkow, M. *Chimia* **1993**, *47*, 19.

(4) Schwesinger, R. *Nachr. Chem. Tech. Lab.* **1990**, *38*, 1214.

(5) Amberg, W.; Seebach, D. *Chem. Ber.* **1990**, *123*, 2429.

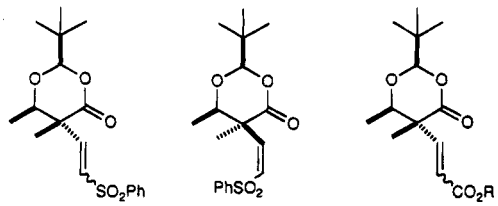
(6) Bulliard, M.; Zehnder, M.; Giese, B. *Helv. Chim. Acta* **1991**, *74*, 1600.

(7) (a) Angeletti, E.; Montanari, F.; Negrini, A. *Gazz. Chim. Ital.* **1957**, *87*, 1086. (b) Shainyan, B. A.; Mirskova, A. N. *Zh. Org. Khim.* **1989**, *25*, 68.

(8) (a) Ma, S.; Lu, X. *Org. Synth.* **1993**, *72*, 112. (b) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475.

(9) LDA is not compatible with this reaction sequence owing to the rapid competing addition of diisopropylamine to the bromovinyl sulfones and bromoacrylates.

0022-3263/94/1959-7921$04.50/0



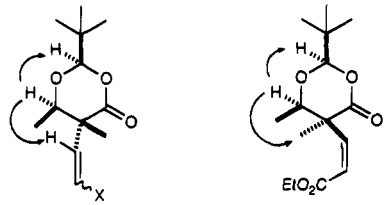
17: E
18: Z

19

20: E, R = Me
21: Z, R = Et

with the Z-bromovinyl sulfone **12** was slow and the reaction was incomplete even after 24h at −78 °C. Moreover, this reaction was much less selective and resulted in the isolation of **18** and **19** in 52% combined yield and a ratio of 1.6:1. A similar phenomenon was observed for the bromoacrylates whereby quenching with **16** was clean and gave **20** in 71% isolated yield and excellent diasteroselectivity (>20:1) but that with **15** was much slower, lower yielding (51% isolated) and gave a mixture of diastereomers (**21**:**22** = 6:1) together with recovered substrate.

It seems apparent that both *E*-bromovinyl sulfones and *E*-bromoacrylates react cleanly and rapidly with the lithium enolate of **3** and with the anticipated selectivity, anti to the 6-Me substituent. On the other hand, for the *Z*-isomers attack anti the to 6-Me group is apparently hindered, leading to longer reaction times and eventual competition from attack syn to the 6-Me group. It is noteworthy that regardless of the configuration, *E*- or *Z*-, of the electrophile in each of the above reactions it was cleanly retained in the addition/elimination process in accord with previous studies of nucleophilic attack on β-bromovinyl sulfoxides.[10] In each of the derivatives **17**, **18**, **20**−**22** the relative configuration at the dioxanone C-5 was solved by means of NOE. difference spectroscopy as indicated in Figure 1. In the case of **22**, for which a pure sample was not available, the NOE experiment was conducted on a mixture with **21**.

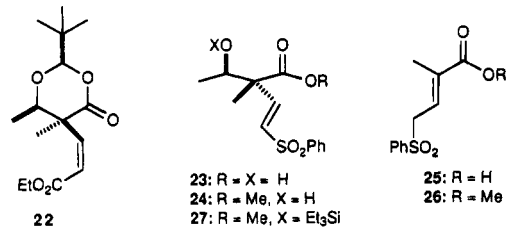


17: X= E-SO2Ph
18: X= Z-SO2Ph
20: X = E-CO2Me
21: X = Z-CO2Et

22

Figure 1.

With an efficient synthesis of **17** in hand we turned to cleavage of the dioxane ring. Treatment of **17** with 3N HCl in THF for 24h followed by evaporation to dryness gave a sample of the acid **23** free from any major impurities. Unfortunately, attempted purification of **23**, as described by Seebach for related compounds, by extraction into Na_2CO_3 and subsequent reacidification resulted in slow retroaldolization with increasing contamination of **23** by the α,β-unsaturated acid **25**. Methanolysis of **17** with HCl in MeOH overnight enabled the isolation of the ester **24** in 96% yield. Attempted purification of **24** by chromatography on silica gel again resulted in retroaldolization and the isolation of **26** as the pure *E*-isomer.[11] Evidently, the extra conjugation afforded any enol or enolate on cleavage of **23** and **24**, by the vinyl sulfone is sufficient to promote the retroaldol reaction under conditions in which the saturated derivatives studied by Seebach were stable. Eventually the problem of purification and stability was solved by silylation of crude **24** under standard conditions giving **27** in excellent yield.



22

23: R = X = H
24: R = Me, X = H
27: R = Me, X = Et3Si

25: R = H
26: R = Me

In conclusion we have provided useful methodology for the preparation of diastereomerically pure α-vinyl-α-alkyl-β-hydroxy esters from the simple β-hydroxy esters which themselves are available with high enantiomeric purity by a number of methods, for instance by aldol condensation reactions,[12] and by microbial reduction[13] and catalytic hydrogenation[14] of β-keto esters. In addition we have demonstrated the dependence of stereoselectivity of the central Michael addition/elimination sequence on geometry of the electrophile with *E*-bromovinyl sulfones and *E*-bromoacrylates giving excellent selectivity and the *Z*-isomers much less so. Application of this chemistry in total synthesis is currently underway and will be reported in due course.

Experimental Section

All solvents were dried and distilled by standard procedures. Unless otherwise stated all reactions were run under a dry nitrogen or argon atmosphere. THF was distilled, under N_2, immediately prior to use from sodium benzophenone ketyl. ^1H and ^{13}C-NMR spectra were run in $CDCl_3$ at 300 and 75 MHz respectively. IR spectra were recorded as $CHCl_3$ or CH_2Cl_2 solutions. Microanalyses were performed by Midwest Microlabs, Indianapolis, IN.

(*Z*)-(2-Bromovinyl) Phenyl Sulfone (12). (*Z*)-(2-Bromovinyl) phenyl sulfide (**11**)[7a] (2.151 g, 0.01 mol) was dissolved in THF (20 mL) and magnesium monoperoxyphthalate (7.420 g, 0.015 mol) was added portionwise. The reaction mixture was stirred at room temperature 48 h. After completion (TLC), $CHCl_3$ (100 mL) was added and the resulting precipitate filtered off and washed several times with $CHCl_3$. The organic layer was washed with sat. sodium bicarbonate (50 mL), water (2 × 100 mL) and sat. sodium chloride (50 mL), dried ($MgSO_4$) and evaporated *in vacuo*. The oily product was purified by column chromatography on silica gel (eluent, diethyl ether:pentane = 1:3) yielding 2.076 g (84%) of the white crystalline sulfone (**12**): mp 39−40 °C (lit.[7a] mp 41−42 °C); δ_H 7.12 (d, 1H, J = 8.2 Hz), 7.21 (d, 1H, J = 8.2 Hz), 7.55 (t, 2H, J = 7.6 Hz), 7.66 (m, 1H), 7.96−8.02 (m, 2H); δ_C 121.10, 128.00, 129.17, 134.01, 135.79, 139.95; IR 1575, 1326, 1152 cm^{-1}.

(*E*)-(2-Bromovinyl) Phenyl Sulfone (14). (*Z*)-(2-Bromovinyl) phenyl sulfone (**12**) (0.365g, 1.48 mmol) was dissolved in CCl_4 (20 mL) and Br_2 (cat., 1 drop) was added. The reaction mixture was irradiated with a 250 W sunlamp for 5 min after which the orange color of the solution had dissipated. The solvent was evaporated *in vacuo* and residue was purified by column chromatography on silica gel (eluent, diethyl ether: pentane = 1:3) yielding the yellowish crystalline product (**14**)

(10) Hori, I.; Oishi, T. *Tetrahedron Lett.* **1979**, 4087 and references therein.

(11) Assigned by NOE difference spectroscopy.

(12) (a) Evans, D. A.; Bartoli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Corey, E. J.; Lee, D.-H. *Tetrahedron Lett.* **1993**, *34*, 1737.

(13) Sih, C. J.; Chen, C.-S. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 570.

(14) Noyori, R.; Ohkuma, T.; Kitamura, M.; Tukaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856.

(0.345 g, 94%): mp 55–56 °C (lit.[7a] mp 58–60 °C); δ_H 6.99 (dd, 1H, J = 13.5, 2.8 Hz), 7.52–7.59 (m, 2H), 7.62–7.71 (m, 2H), 7.85–7.91 (m, 2H); δ_C 124.46, 127.80, 129.52, 133.99, 136.94, 139.22; IR 1585, 1326, 1148 cm^{-1}.

General Procedure for Michael Addition/Elimination Reactions of Vinyl Bromides with 3. A solution of lithium bis(trimethylsilyl)amide[9] was prepared by dropwise addition under Ar of a solution of butyllithium (0.46 mL, 0.93 mmol of 2 M solution in pentane) into a solution of bis(trimethylsilyl)amine (161 mg, 0.21 mL, 1 mmol) in dry THF (1.5 mL) chilled to 0–5 °C followed by stirring for 20 min. A solution of **3** (150 mg, 0.805 mmol) in dry THF (1.5 mL) was added dropwise into a solution of lithium bis(trimethylsilyl)amide (0.46 mL, 0.93 mmol) chilled to −78 °C. The reaction mixture was stirred 45 min at this temperature before a solution of the vinyl bromide (1.1 mmol) in dry THF (1mL) was added. The reaction mixture was then stirred at −70 to −78 °C 24 h and then warmed up to room temperature within 1 h followed by quenching with sat. ammonium chloride (5 mL), separation of the organic layer and ether extraction of the aqueous layer (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$) and evaporated *in vacuo*. The oily residue was purified by chromatography on silica gel typically eluting with pentane: diethyl ether (4:1) to yield a colorless oil which solidified on standing.

(±)-(2*R*,5*R*,6*R*)-2-*tert*-Butyl-5,6-dimethyl-5-[2(*E*)-(phenylsulfonyl)vinyl]-1,3-dioxan-4-one (17). Reaction of **3** with **14** according to the standard protocol gave **17** as a single diastereomer in 65% isolated yield: mp 105–106 °C; δ_H 0.97 (s, 9H), 1.20 (d, 3H, J = 6.4 Hz), 1.37 (s, 3H), 4.01 (q, 1H, J = 6.4 Hz), 4.99 (s, 1H), 6.58 (d, 1H, J = 15.3 Hz), 6.90 (d, 1H, J = 15.3 Hz), 7.50–7.58 (m, 2H), 7.63 (tt, 1H, J = 1.4, 7.2 Hz), 7.84–7.90 (m, 2H); δ_C 14.68, 17.02, 23.73, 35.33, 49.40, 75.69, 109.21, 127.71, 129.38, 133.57, 133.64, 139.66, 143.26, 170.59; IR 1738, 1324, 1151 cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86. Found: C, 61.36; H, 6.93.

(±)-(2*R*,5*R*,6*R*)-2-*tert*-Butyl-5,6-dimethyl-5-[2(*Z*)-(phenylsulfonyl)vinyl]-1,3-dioxan-4-one (18) and *rel*-5*S* Diastereoisomer (19). Reaction of **3** with **12** according to the standard protocol gave a 1.6:1 mixture of **18** and **19** in 52% combined isolated yield. Separation by preparative TLC gave a pure sample of the major diastereomeric sulfone **18**, a white crystalline solid: mp 115–117 °C; δ_H 1.02 (s, 9H), 1.21 (d, 3H, J = 6.4 Hz), 1.50 (s, 3H), 4.67 (q, 1H, J = 6.4 Hz), 5.35 (s, 1H), 6.03 (d, 1H, J = 12 Hz), 6.28 (d, 1H, J = 12.9 Hz), 7.50–7.58 (m, 2H), 7.64 (tt, 1H, J = 1.4, 7.1 Hz), 7.95–8.02 (m, 2H); δ_C 15.38, 22.22, 23.95, 34.99, 48.01, 77.43, 108.20, 128.23, 129.27, 131.32, 134.11, 139.09, 143.45, 172.62; IR: 1734, 1310, 1154 cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86. Found: C, 61.40; H, 6.93. The minor diastereomer (**19**) was not obtained pure and the spectral charateristics were taken from a mixture with **18**: δ_H 0.96 (s, 9H), 1.31 (d, 3H, J = 6.5 Hz), 1.77 (s, 3H), 3.88 (q, 1H, J = 6.5 Hz), 4.99 (s, 1H), 6.07 (d, 1H, J = 12.9 Hz), 6.49 (d, 1H, J = 12 Hz), 7.50–7.58 (m, 2H), 7.64 (tt, 1H, J = 1.4, 7.1 Hz), 7.91–7.98 (m, 2H); δ_C 16.43, 20.78, 23.70, 34.93, 51.00, 79.68, 108.89, 127.58, 131.26, 133.51, 134.81, 139.19, 169.85.

(±)-(2*R*,5*R*,6*R*)-2-*tert*-Butyl-5,6-dimethyl-5-[2(*E*)-(methoxycarbonyl)vinyl]-1,3-dioxan-4-one (20). Reaction of **3** with **16** according to the standard protocol gave **20** as a single diastereomer in 71% isolated yield: mp 78–80 °C (ether/pentane); δ_H 0.97 (s, 9H), 1.16 (d, 3H, J = 6.4 Hz), 1.39 (s, 3H), 3.73 (s, 3H), 3.97 (q, 1H, J = 6.4 Hz), 4.98 (s, 1H), 6.03 (d, 1H, J = 16 Hz), 6.85 (d, 1H, J = 16 Hz); δ_C 14.60, 16.67, 23.85, 35.32, 49.64, 51.72, 76.08, 109.05, 123.77, 145.46, 166.11, 171.48; IR: 1734, 1213, 985 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 61.98; H, 8.10.

(±)-(2*R*,5*R*,6*R*)-2-*tert*-Butyl-5,6-dimethyl-5-[2(*Z*)-(ethoxycarbonyl)vinyl]-1,3-dioxan-4-one (21) and *rel*-5*S* Diastereoisomer (22). Reaction of **3** with **15** according to the standard protocol gave a 6:1 mixture of **21** and **22** in 51% combined isolated yield. Preparative TLC then crystallization from pentane gave a pure sample of the major diastereomeric ester **21**, a white crystalline solid: mp 62–64 °C (pentane); δ_H 1.00 (s, 9H), 1.14 (d, 3H, J = 6.4 Hz), 1.25 (t, 3H, J = 7.2 Hz), 1.45 (s, 3H), 4.10–4.24 (m, 2H) 4.35 (q, 1H, J = 6.4 Hz), 5.28 (s, 1H), 5.98 (s, 2H); δ_C 14.10, 15.68, 21.42, 23.98, 34.99, 48.47, 60.60, 75.08, 107.72, 122.66, 148.37, 165.47, 172.40; IR 1734, 1712, 1372, 1213 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.29; H, 8.60. The minor diastereomer (**22**) was not obtained pure and the spectral charateristics were taken from a mixture with **21**: δ_H 0.98 (s, 9H), 1.23 (d, 3H, J = 6.4 Hz), 1.28 (t, 3H, J = 7.2 Hz), 1.49 (s, 3H), 3.70 (q, 1H, J = 6.4 Hz), 4.10–4.24 (m, 2H) 4.98 (s, 1H), 5.91 (d, 1H, J = 13.0 Hz), 6.03 (d, 1H, J = 13.0 Hz); δ_C 14.10, 15.76, 18.90, 23.68, 35.26, 50.65, 60.63, 79.37, 108.89, 124.51, 136.79.

(±)-(2*R*,1'*R*)-2-(1-Hydroxyethyl)-2-methyl-4-(phenylsulfonyl)-3(*E*)-butenoic Acid (23). To a solution of the dioxanone **17** (0.178 g, 0.51 mmol) in THF (10 mL) was added 3N HCl (6 mL). The reaction mixture was stirred at room temperature 24 h until hydrolysis was complete (TLC). After extraction with diethyl ether (3 × 5 mL), the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*, yielding 0.140 g (98%) of the oily acid: δ_H 1.06 (d, 3H, J = 6.4), 1.24 (s, 3H), 4.14 (q, 1H, J = 6.4 Hz), 5.81 (bs, 2H), 6.47 (d, 1H, J = 15.4 Hz), 7.09 (d, 1H, J = 15.4 Hz), 7.54 (t, 2H, J = 7.2 Hz), 7.60 (t, 1H, J = 7.2 Hz), 7.83 (d, 2H, J = 7.4 Hz); δ_C 15.11, 17.71, 53.78, 71.57, 127.52, 129.39, 131.39, 133.71, 139.44, 146.03, 175.65; IR: 3480, 1756, 1711, 1323, 1239 cm^{-1}. Any attempt at further purification of this acid, for example by extraction into aqueous Na_2CO_3, resulted only in contamination with 2-methyl-4-(phenylsulfonyl)-2-butenoic acid (**25**): δ_H 1.61 (s, 3H), 4.00 (d, 2H, J = 8.2 Hz), 6.78 (tq, 1H, J = 1.2, 8.2 Hz), 7.58 (t, 2H, J = 7.6 Hz), 7.69 (t, 1H, J = 7.6 Hz), 7.88 (d, 2H, J = 7.6 Hz); δ_C 12.33, 56.32, 128.32, 128.5, 128.39, 134.18, 135.13, 138.33, 171.32.

(±)-Methyl (2*R*,1'*R*)-2-(1-Hydroxyethyl)-2-methyl-4-(phenylsulfonyl)-3(*E*)-butenoate (24). The dioxanone **17** (86.4 mg, 0.245 mmol) was dissolved in a saturated solution of HCl in MeOH (4 mL) and the reaction mixture stirred at room temperature 20 h until hydrolysis was complete (TLC). The solvent was then evaporated *in vacuo* to give 70.1 mg (96%) of the oily methyl ester **24**: δ_H 1.16 (d, 3H, J = 6.5), 1.32 (s, 3H), 2.85 (bs, 1H), 3.73 (s, 3H), 4.14 (q, 1H, J = 6.5 Hz), 6.42 (d, 1H, J = 15.4 Hz), 7.08 (d, 1H, J = 15.4 Hz), 7.51–7.59 (m, 2H), 7.64 (tt, 1H, J = 7.4, 1.4 Hz), 7.85–7.90 (m, 2H); δ_C 15.64, 18.02, 52.69, 53.80, 71.46, 127.55, 129.30, 131.59, 133.52, 139.93, 145.68, 173.53; IR: 3689, 1719, 1606, 1258 cm^{-1}.

Methyl 2-Methyl-4-(phenylsulfonyl)-2(*E*)-butenoate (26). Attempted purification of **24** by chromatography on silica gel (eluent, diethyl ether:pentane = 1:2) resulted only in the isolation of the retroaldol product **26**, as a crystalline solid: mp 80–81 °C (lit.[15] mp 73 °C); δ_H 1.56–1.59 (broad s, 3H), 3.74 (s, 3H), 3.96 (dd, 2H, J = 8.2, 0.5 Hz), 6.66 (tq, 1H, J = 8.2, 1.6 Hz), 7.52–7.59 (m, 2H,), 7.68 (tt, 1H, J = 7.4, 1.4 Hz), 7.84–7.90 (m, 2H); δ_C 12.54, 52.21, 56.21, 126.09, 128.28, 129.31, 134.06, 135.77, 138.39, 167.04; IR: 1718, 1294, 1146 cm^{-1}.

(±)-Methyl (2*R*,1'*R*)-2-(1-Triethylsiloxyethyl)-2-methyl-4-(phenylsulfonyl)-3(*E*)-butenoate (27). To a solution of crude hydroxy ester **24** (20.4 mg, 0.068 mmol) in anhydrous CH_2Cl_2 (1 mL) was added imidazole (18.5 mg, 0.272 mmol) then triethylsilyl chloride (22.8 μL, 0.136 mmol) resulting in the immediate formation of a precipitate. After completion (TLC, 1.5 h) the reaction mixture was diluted with CH_2Cl_2 (5 mL) and washed with sat. solution of NH_4Cl (2 mL), brine (2 mL), dried ($MgSO_4$) and the solvent evaporated *in vacuo*. The silyl ether **27** was obtained as a colorless oil (23.1 mg, 82%) after preparative TLC on silica gel (eluent, pentane:ethyl acetate 2:1): δ_H 0.52 (q, 6H, J = 7.7 Hz), 0.89 (t, 9H, J = 7.7 Hz), 1.03 (d, 3H, J = 6.3 Hz), 1.29 (s, 3H), 3.69 (s, 3H), 4.25 (q, 1H, J = 6.3 Hz), 6.40 (d, 1H, J = 15.4 Hz), 7.15 (d, 1H, J = 15.4 Hz), 7.50–7.57 (m, 2H), 7.62 (tt, 1H, J = 7.3, 1.4 Hz), 7.83–7.89 (m, 2H); δ_C 4.95, 6.72, 15.55, 19.12, 52.38, 54.82, 72.46, 127.61, 129.27, 131.54, 133.39, 140.31, 146.01, 172.92; IR 1733, 1622, 1250, 1150 cm^{-1}. Anal. Calcd for $C_{20}H_{32}O_5SSi$: C, 58.22; H, 7.82. Found: C, 58.31; H, 7.77.

Acknowledgment. We thank the University of Illinois at Chicago for support of this work and for Graduate Fellowships to M.B.

Supplementary Material Available: 300 MHz ^{1}H NMR of **17**, **18**, **20**, **21**, **23**, **24**, **26**, and **27**, of **19** in admixture with **18**, and of **22** in admixture with **21** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(15) Mamescalchi, F.; Orena, M.; Savoia, D. *Synthesis* **1979**, 445.