Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 04 Dec 2007.

To cite this article: Leonid N. Koikov, Mingming Han, Dawn M. Wellman, Jim A. Kelly & Irina P. Smoliakova (2000) The Use of tert-Butyl Vinyl Ether in Stepwise Electrophilic Addition Reactions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:18, 3451-3464, DOI: 10.1080/00397910008086984

To link to this article: http://dx.doi.org/10.1080/00397910008086984

SYNTHETIC COMMUNICATIONS, 30(18), 3451–3464 (2000)

THE USE OF *tert*-BUTYL VINYL ETHER IN STEPWISE ELECTROPHILIC ADDITION REACTIONS

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Abstract: *tert*-Butyl vinyl ether (1) reacts with *p*-TolSCl to give 2-*tert*-butoxy-2-chloroethyl *p*-tolyl sulfide (**2**). In the presence of $SnCl_4$, **2** reacts with silyl enol ethers, allyltrimethylsilane, and vinyl ethers to form a C-C bond. In the case of vinyl ethers, the reaction proceeds through the formation of the 5-membered sulfonium salt intermediate which in turn can react with H_2O, TMSCN, allyltrimethylsilane, and Grignard reagents.

It has been reported that vinyl ethers are excellent substrates for stepwise electrophilic addition proceeding through episulfonium ions (ESIs) as intermediates (Scheme 1).[1] We have also described that vinyl ethers can be used as nucleophiles (Nu) in the reactions with ESIs.[1,2] In this case, the reaction takes place through a five-membered sulfonium salt intermediate, the structure of which was established by X-ray crystallographic analysis.[3] The intermediate reacts with a number of nucleophiles including H_2O, MeOH, *n*-Bu_4NBH_4, Grignard reagent, and silyl enol ethers (Scheme 2).[1-3] So far, among acyclic derivatives, only methyl vinyl ethers have been employed in both steps of the reaction.

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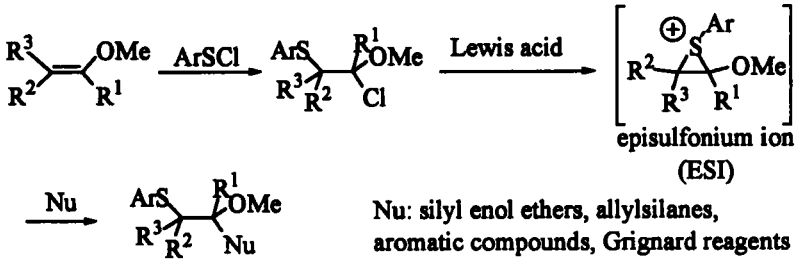
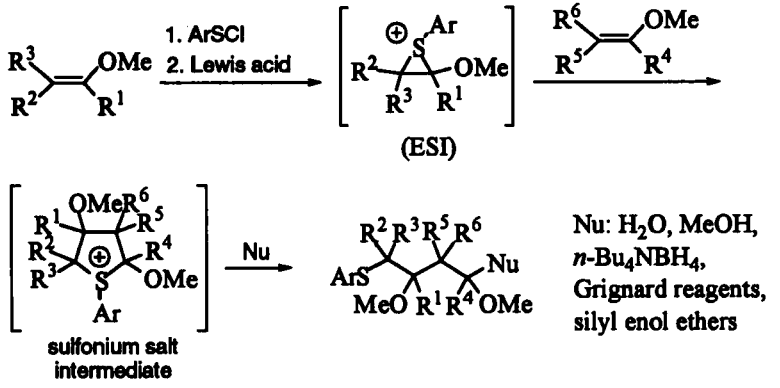


Scheme 1

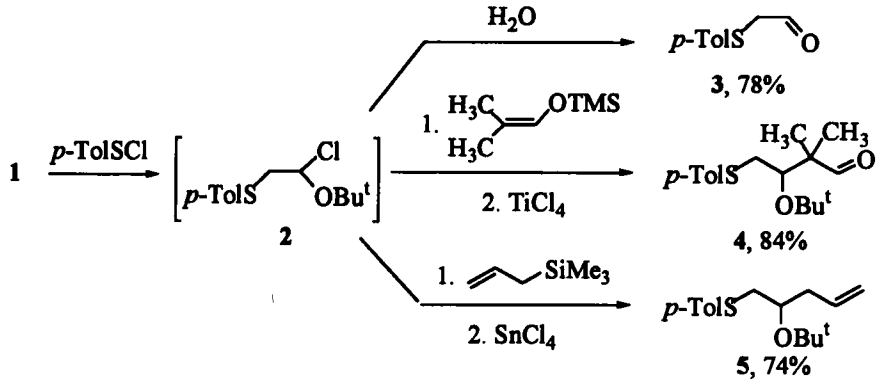


Scheme 2

tert-Butyl vinyl ether (**1**) is a valuable and versatile reagent for a number of reasons. The presence of bulky groups, e.g., the *tert*-butyl group, often improves the regio- and stereoselectivity of reactions.[4] Also, *tert*-butoxy substituted compounds can be converted to the corresponding hydroxy derivatives by removal of the *tert*-butyl group.[5] Compared to methyl vinyl ether, **1** is easier to handle because it is a liquid at room temperature. In spite of these advantages, **1** has been used preferentially in cycloaddition reactions, including Diels-Alder reactions,[6] and

in the synthesis of a number of polymers.[7] There are only limited data on electrophilic addition of ethanol, bromine, and carboxylic acids to the vinyl ether.[8] In this paper, we disclose our results on the use of **1** in stepwise electrophilic addition reactions.

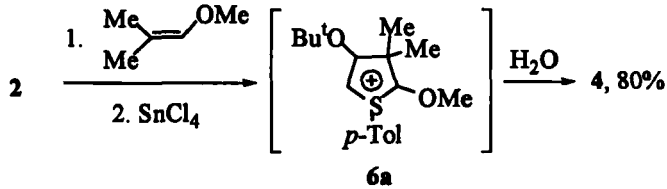
We have found that **1** readily reacted with *p*-TolSCl in CH_2Cl_2 at -78 °C to afford 2-*tert*-butoxy-2-chloroethyl *p*-tolyl sulfide (**2**) in quantitative yield (^{1}H NMR data). This compound is stable in CH_2Cl_2 at -78 °C for several hours, but it quickly decomposes at room temperature. Reaction of **2** with H_2O afforded 2-(*p*-tolylthio)ethanal (**3**) in 78% yield. In the presence of a Lewis acid, adduct **2** was capable of reacting with 2-methyl-1-(trimethylsilyloxy)-1-propene and allyltrimethylsilane to form compounds **4** and **5** in yields of 84% and 74%, respectively (Scheme 3).



Scheme 3

As expected, adduct **2** reacted with vinyl ethers as well. Thus, compound **4** was synthesized using 1-methoxy-2-methyl-1-propene as a C-Nu and H_2O as a quenching nucleophile (Scheme 4). By analogy with the known reactions of methyl

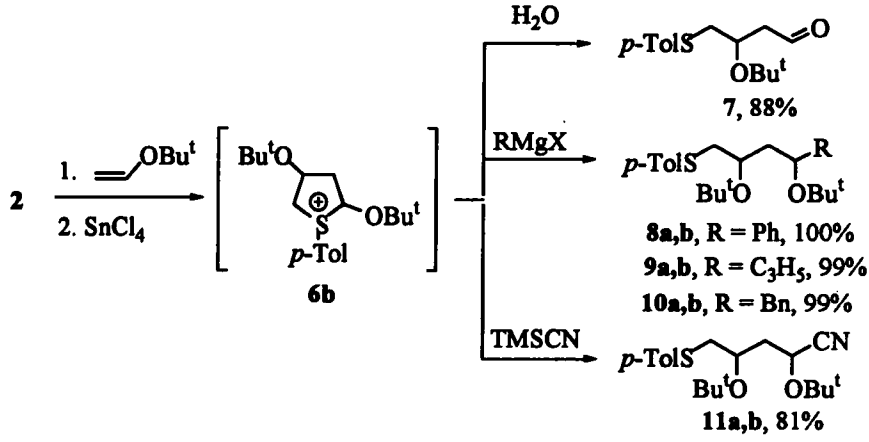
vinyl ether,[2,3] we suggest that the reaction proceeds through formation of a sulfur-stabilized cyclic intermediate (**6a**). In the presence of $SnCl_4$, adduct **2** also reacted with **1**. The intermediate was quenched with a number of different nucleophiles: H_2O, PhMgBr, allylmagnesium bromide, BnMgCl, and TMSCN (Scheme 5). In contrast to the previously studied reactions of less sterically hindered cyclic sulfonium salts,[2d,e] Grignard reagents reacted not only with the bulky **6b** but also with $SnCl_4$ to form Ph_3SnOH or Bn_4Sn. The use of 6 molar excess of Grignard reagents in the reactions with **6b** lead to the preparation of desired compounds **8-10** in quantitative yield. When the reaction mixtures were quenched with a mixture of aq. $NaHCO_3$ and ether, a partial deprotection of the *tert*-butyl groups occurred and the mixtures of di- and mono-*tert*-butyl derivatives were formed. The change of ether for less water miscible CH_2Cl_2 allowed the preparation of **8–11** in quantitative yield.



6a

Scheme 4

Compounds **8**, **9**, and **10** were isolated as stereoisomeric mixtures of *erythro* and *threo* isomers (1.3:1, 5.4:1, and 1.9:1, respectively). In all the cases the isomers were separated by column chromatography. The relative configurations



Scheme 5

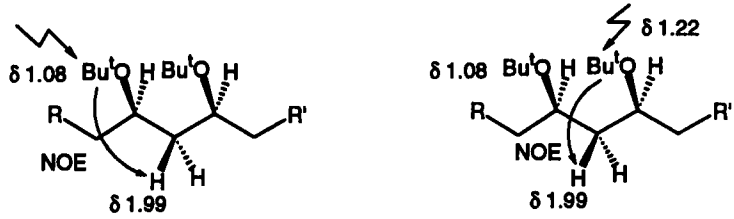


Figure 1. Results of two NOE experiments for ***erythro*-10**.

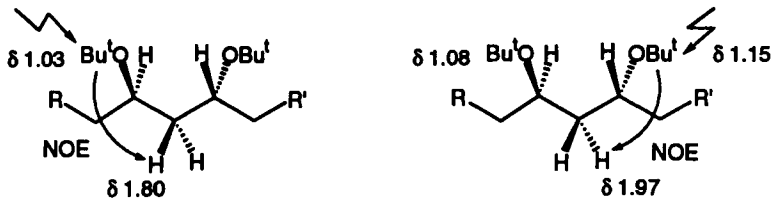
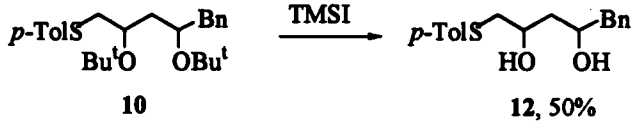


Figure 2. Results of two NOE experiments for ***threo*-10**.

Nitrile **11** also was obtained as a stereoisomeric mixture (1:7) with the major isomer (***threo*-11**) having a lower value of R_f. In a solution of $CDCl_3$, ***erythro*-11** and ***threo*-11** each isomerized back to the 1:7 stereoisomeric mixture. Thus, the 1:7 ratio reflects relative thermodynamic stability of the isomers in this solvent.

The use of other Lewis acids, $TiCl_4$, $CuBr_2$, and $ZnCl_2$, did not significantly improve the stereoselectivity of the reactions depicted in Scheme 5.

Synthesis of 1,3-diols from the di-*tert*-butoxy derivatives turned out to be troublesome. The use of CF_3CO_2H, 5% CF_3CO_2H in CH_2Cl_2, and $FeCl_3$ in acetone provided the mixtures of 1,3-diols and their monoprotected derivatives which were unstable during chromatographic separation. Treatment of pure ***erythro*-10** and ***threo*-10** with TMSI provided the corresponding *erythro* and *threo* 1,3-diols (***erythro*-12** and ***threo*-12**) in a yield of 50% for each reaction after chromatographic separation. Control of time and temperature of the reaction were important. Thus, the reaction of TMSI with ***erythro*-10** at –20 °C was complete within 10-15 min. Increased reaction time significantly reduced the yield of diols. When the reaction was carried out at –78 °C, only traces of the products were detected after one hour. Our attempt to deprotect the mixture of ***erythro*-10** and ***threo*-10** and separate the resulting isomeric diols failed because the R_f values of ***erytro*-12** and ***threo*-12** were the same.



10 **12, 50%**

Scheme 6

In summary, we have shown that *tert*-butyl vinyl ether can be successfully used in stepwise electrophilic addition reactions proceeding through episulfonium-like or sulfonium-like intermediates. The latter react with Grignard reagents to afford isomeric mixtures of 1,3-di-*tert*-butoxyalkane derivatives in quantitative yield. These isomers can be easily separated and converted to the corresponding 1,3-diols using TMSI.

Experimental

^1H and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded in $CDCl_3$. Coupling constants, *J*, are reported in Hz. IR spectra (neat) were recorded on an ATI Mattson Genesis Series FTIR spectrometer. DCI-HRMS were obtained on a VG 7070 high resolution mass spectrometer. Preparative TLC were carried out by using glass plates, 200 x 200 mm, with an unfixed layer (2.5 mm) of Merck silica gel 60 (230-400 mesh). Analytical TLC and flash chromatography were performed on Whatman PE Sil G/UV plates and silica gel 60, respectively. All of the reactions were carried out under an atmosphere of dry nitrogen using flame-dried glassware and freshly distilled and dried solvents.

p-Tolylsulfenyl chloride was obtained from the corresponding thiophenol using SO_2Cl_2.[9] Methyl vinyl ether was synthesized from *n*-butyl vinyl ether and MeOH in the presence of $Hg(OAc)_2$.[10] 1-Methoxy-2-methyl-1-propene was prepared by pyrolysis of 1,1-dimethoxy-2-methylpropane using *p*-toluenesulfonic acid as a catalyst.[11] Other reagents were supplied by Aldrich Chemical Co.

3-*tert*-Butoxy-2,2-dimethyl-4-(*p*-tolylthio)butanal (4). To a solution of 0.317 g (2 mmol) *p*-TolSCl in 20 mL CH_2Cl_2 at -78 °C was added 0.28 mL (2 mmol) *tert*-butyl vinyl ether. Then 0.5 mL (4 mmol) 2-methyl-1-(trimethylsilyloxy)-1-propene and 2.4 mL of 1 M solution (2.4 mmol) of $SnCl_4$ in CH_2Cl_2 were introduced sequentially. The mixture was stirred at -78 °C for 1 h,

quenched with aqueous saturated $NaHCO_3$, extracted with CH_2Cl_2, and dried over K_2CO_3. After solvent removal, preparative TLC (ether/hexane, 1:7) afforded pure compound **4** as colorless oil (0.493 g, 84%). This compound was obtained in a yield of 80% following the same procedure but using 1-methoxy-2-methyl-1-propene instead of 2-methyl-1-(trimethylsilyloxy)-1-propene. In both reactions, a small amount (up to 5%) of 2,2-dimethyl-3-hydroxy-4-(*p*-tolylthio)butanal was isolated as well. Data for **4**: R_f 0.36 (hexane/ethyl acetate, 7:1). ^1H NMR (δ, 200 MHz): 1.04 (s, 6H), 1.13 (s, 9H), 2.29 (s, 3H), 2.99, 3.07 (2 dd, $J_1 = 3.9$, $J_2 = 6.3$, $J_3 = 13.7$), 3.77 (dd, 1H, $J_1 = 3.9$, $J_2 = 6.3$), 7.16 (m, 4H), 9.65 (s, 1H). ^{13}C NMR (δ, 50 MHz): 18.0, 18.6, 18.6, 27.9, 37.8, 49.6, 73.8, 74.0, 129.0, 129.9, 131.8, 135.8, 203.7. IR (neat): 1716 cm^{-1}. HRMS: calcd. for $C_{17}H_{26}SO_2$ (M^+) m/z 294.1653, found 294.1651.

4-*tert*-Butyl-5-(*p*-tolylthio)-1-pentene (5) was synthesized according to the procedure given for compound **4** using allyltrimethylsilane (4 mmol) and $TiCl_4$ (2.2 mmol). Yield is 0.445 g (74%). Up to 10% of 4-hydroxy-5-(*p*-tolylthio)-1-pentene was isolated as well. Data for **5**: R_f 0.65 (hexane/ethyl ether, 5:1). ^1H NMR (δ, 200 MHz): 1.05 (s, 6H), 1.13 (s, 9H), 2.20 (s, 3H), 2.21 (m, 2H), 2.85, 2.87 (2 dd, 2H, $J_1 = 5.3$, $J_2 = 7.0$, $J_3 = 13.2$), 3.57 (m, 1H), 4.98 (m, 2H), 5.74 (m, 1H), 7.16 (m, 4H). ^{13}C NMR (δ, 50 MHz): 20.9, 28.5, 39.7, 39.9, 70.0, 74.0, 117.2, 129.5, 130.0, 133.0, 134,6, 135.9, 203.7. IR (neat): 1640 cm^{-1}. HRMS: calcd. for $C_{16}H_{24}SO$ (M^+) m/z 264.1548, found 264.1550.

3-*tert*-Butoxy-4-(*p*-tolylthio)butanal (7). To a solution of 0.079 g (0.5 mmol) *p*-TolSCl in 10 mL CH_2Cl_2 at -78 °C were sequentially added 1.25 mL of 1 M solution of *tert*-butyl vinyl ether (0.125 g, 1.25 mmol) and 0.6 mL of 1 M solution of $SnCl_4$ (0.6 mmol). The mixture was stirred at -78 °C for 3 h, quenched with a mixture of 5% aqueous $NaHCO_3$ and CH_2Cl_2, extracted with CH_2Cl_2, and

dried over K_2CO_3. After solvent removal, flash chromatography (hexane/ether, 8.5:1) afforded pure compound **7** as colorless oil (0.117 g, 88%). R_f 0.63 (toluene/ether, 1:1). ^1H NMR (δ, 300 MHz): 1.09 (s, 9H), 2.27 (s, 3H), 2.60, 2.78 (2 ddd, 2H, J_1 = 1.9, J_2 = 2.4, J_3 = 5.5, J_4 = 6.0, J_5 = 16.1), 2.87, 3.09 (2 dd, 2H, J_1 = 4.5, J_2 = 8.4, J_3 = 13.5), 4.09 (m, 1H), 7.16 (m, 4H), 9.72 (br. t, 1H). ^{13}C NMR (δ, 50 MHz): 20.6, 28.0, 40.7, 49.0, 63.1, 74.4, 129.4, 130.3, 131.7, 136.2, 200.6. IR (neat): 1728 cm^{-1}. HRMS: calcd. for $C_{15}H_{22}SO_2$ (M^+) m/z 266.1340, found 266.1342.

***erythro-* and *threo*-1,3-Di-*tert*-butoxy-1-phenyl-4-(*p*-tolylthio)butane (*erythro*-8 and *threo*-8).** To a solution of 0.159 g (1 mmol) *p*-TolSCl in 20 mL CH_2Cl_2 at -78 °C were sequentially added 2.5 mL of 1 M solution of *tert*-butyl vinyl ether (2.5 mmol) and 1.2 mL of 1 M solution of $SnCl_4$ (1.2 mmol). After 30 min, 2 mL of 3 M solution of PhMgBr (6 mmol) diluted with 4 mL of anhydrous ether[b] was added. The mixture was stirred at -78 °C for 3 h and then left overnight at room temperature. After cooling to 0 °C, the mixture was quenched with 5% aqueous $NaHCO_3$, extracted with CH_2Cl_2, and dried over K_2CO_3. After CH_2Cl_2 removal, the residue was extracted with hexane to remove Ph_3SnOH as a colorless solid, m.p. 113-115 °C (lit.[12] m.p. 118 °C). After hexane removal, the crude product was purified by column chromatography (hexane/ether, 20:1) providing 0.384 g (quantitative yield) of the mixture of ***erythro*-8** and ***threo*-8** in a ratio of 1.3:1, respectively (^1H NMR data). The use of $TiCl_4$ (0.114 g, 1.2 mmol) instead of $SnCl_4$ gave the mixture of ***erythro*-8** and ***threo*-8** (0.179 g, 92%) in a ratio of 2.6:1, respectively (^1H NMR data). R_f (hexane/ether, 15:1) 0.46 and 0.32, respectively. Data for ***erythro*-8**: ^1H NMR (δ, 300 MHz): 1.12, 1.16 (2 s, 18H), 2.01 (m, 2H), 2.31 (s, 3H), 3.10, 3.22 (2 dd, 2H, J_1 = 5.1, J_2 =

[b] Without dilution of the viscous solution of the Grignard reagent with diethyl ether, ***erythro*-8** (0.133 g, 34%), ***threo*-8** (0.103 g, 20%), and **7** (0.037 g, 14%) were isolated.

6.2, J_3 = 13.0), 3.82[c] (m, 2H), 4.65 (dd, 1H, J_1 = 4.8, J_2 = 7.5), 7.20 (m, 9H). ^{13}C NMR (δ, 50 MHz): 20.5, 28.1, 28.2, 40.8, 45.8, 67.4, 71.1, 73.3,[c] 125.6, 127.4, 128.8, 129.6, 132.2, 135.1, 145.2, 145.6. HRMS: calcd. for $C_{25}H_{36}SO_2$ (M^+) m/z 400.2436, found 400.2442. Data for ***threo*-8**: ^{1}H NMR (δ, 300 MHz): 1.10, 1.11 (2 s, 18H), 1.94, 2.11 (2 ddd, 1H, J_1 = 3.6, J_2 = 6.5, J_3 = 14.1 and 1H, $J_1 = J_2$ =7.0, J_3 = 14.1), 2.30 (s, 3H), 2.92, 3.01 (2 dd, 2H, J_1 = 4.8, J_2 = 6.3, J_3 = 12.9), 3.68[c] (m, 2H), 4.61 (t, 1H, J = 6.7), 7.25 (m, 9H). ^{13}C NMR (δ, 75 MHz): 21.0, 28.8, 28.9, 41.8, 46.9, 68.6, 72.2, 74.0, 74.3, 126.5, 126.9, 128.1, 129.5, 130.2, 133.8, 135.8, 146.0. HRMS: calcd. for $C_{25}H_{36}SO_2$ (M^+) m/z 400.2436, found 400.2438.

***erythro*- and *threo*-4,6-Di-*tert*-butoxy-7-(*p*-tolylthio)-1-heptene (*erythro*-9 and *threo*-9).** were synthesized using 3 mmol (3 mL of 1 M solution) allylmagnesium bromide by the method described for **8**. Yield is 0.125 g (84%) of ***erythro*-9** and 0.023 g (15%) of ***threo*-9**. R_f 0.35 and 0.26 (hexane/ether, 15:1), respectively. Data for ***erythro*-9**: ^{1}H NMR (δ, 300 MHz): 1.16, 1.18 (2 s, 18H), 1.70, 1.91 (2 ddd, 2H, $J_1 = J_2$ = 5.4, J_3 = 14.0, $J_4 = J_5$ = 6.8), 2.23 (m, 2H), 2.30 (s, 3H); 2.94, 3.05 (2 dd, 2H, J_1 = 4.7 Hz, J_2 = 6.8, J_3 = 13.0), 3.60, 3.70 (2 m, 2H), 5.02 (m, 2H), 5.85 (m, 1H), 7.18 (m, 4H). ^{13}C NMR (δ, 50 MHz): 20.9, 28.8,[c] 41.1, 41.5, 42.6, 68.5, 69.2, 73.5, 74.0, 116.6, 129.5, 130.4, 133.4, 135.4, 136.0. HRMS: calcd. for $C_{22}H_{36}SO_2$ (M^+) m/z 364.2436, found 364.2419. Data for ***threo*-9**: ^{1}H NMR (δ, 300 MHz): 1.16, 1.18 (2 s, 18H), 1.78, 1.88 (2 m, 2H), 2.25 (m, 2H), 2.30 (s, 3H), 3.02, 3.04 (2 m, 2H), 3.60, 3.70 (2 m, 2H), 5.02 (m, 2H), 5.85 (m, 1H), 7.16 (m, 4H). ^{13}C NMR (δ, 75 MHz): 21.1, 28.9, 29.0, 41.6, 41.8, 43.5, 69.2, 69.3, 73.7, 74.2, 116.8, 129.6, 130.3, 133.7, 135.5, 136.0. HRMS: calcd. for $C_{22}H_{37}SO_2$ (MH^+) m/z 365.2514, found 365.2507.

[c] overlapping signal

***erythro*- and *threo*-2,4-Di-*tert*-butoxy-1-phenyl-5-(*p*-tolylthio)pentane (*erythro*-10 and *threo*-10).** were synthesized using 6 mmol (6 mL of 1 M solution) BnMgCl by the method described for **8**. Combined yield of ***erythro*-10** and ***threo*-10** is 99% in a ratio of 1.9:1, respectively. R_f 0.57 and 0.48 (hexane/ether, 7:1), respectively. The use of 2 mmol (2 mL of 1M solution) BnMgCl provided 0.188 g (78%) Bn_4Sn (R_f 0.75, hexane/ether, 7:1, m.p. 40-42 °C, lit.[12] m.p. 42-44 °C), 0.040 g (10%) of the mixture of ***erythro*-10** and ***threo*-10** in a ratio of 2:1 (^{1}H NMR data), and 0.156 g (58%) of **7**. Data for ***erythro*-10**: ^{1}H NMR (δ, 300 MHz): 1.08, 1.22 (s, 18H), 1.80, 1.99 (m, 2H), 2.35 (s, 3H), 2.75, 2.83 (2 dd, 2H, J_1 = 5.4, J_2 = 7.3, J_3 = 13.6), 2.95, 3.07 (2 dd, 2H, J_1 = 4.5, J_2 = 7.2, J_3 = 13.1), 3.78[c] (m, 2H), 7.20 (m, 9H). ^{13}C NMR (δ, 50 MHz): 20.3, 28.0, 28.2, 41.0, 42.4, 42.6, 68.3, 69.7, 73.4, 73.8, 125.3, 127.3, 128.9, 129.3, 129.9, 132.7, 135.5, 139.1. HRMS: calcd. for $C_{26}H_{38}SO_2$ (M^+) m/z 414.2592, found 414.2588. Data for ***threo*-10** ^{1}H NMR (δ, 500 MHz): 1.03, 1.15 (2 s, 18H), 1.80, 1.97 (m, 2H), 2.33 (s, 3H), 2.71, 2.85 (2 dd, 2H, J_1 = 4.9, J_2 = 7.4, J_3 = 13.5), 3.04, 3.07 (2 dd, 2H, J_1 = 5.5, J_2 = 5.6, J_3 = 13.2), 3.73 (m, 2H), 7.20 (m, 9H). ^{13}C NMR (δ, 75 MHz): 21.0, 28.6, 28.8, 41.8, 43.6, 44.1, 69.5, 71.2, 73.7, 74.1, 126.0, 128.0, 129.6, 129.9, 130.2, 133.6, 136.0, 139.5. HRMS: calcd. for $C_{26}H_{38}SO_2$ (M^+) m/z 414.2592, found 414.2590.

***erythro*- and *threo*-2,4-Di-*tert*-butoxy-5-(*p*-tolylthio)pentanenitrile (*erythro*-11 and *threo*-11).** were prepared using 0.8 mmol of TMSCN by the method described for **8**. Yield is 0.017 g (10%) of ***erythro*-11** and 0.12 g (71%) of ***threo*-11**. R_f 0.47 and 0.38 (hexane/ether, 7:1), respectively. Data for a mixture of ***erythro*-11** and ***threo*-11** (ca. 2:1, respectively): ^{1}H NMR (δ, 300 MHz): 1.13, 1.14, 1.27,[c] 1.29[c] (2 s, 18H), 1.98, 2.13[c], 2.29[c] (m, 2H), 2.31[c] (s, 3H), 2.88, 2.94,[c] 3.06, 3.09[c] (2 dd, 2H, J_1 = 5.2, J_2 = 7.8, J_3 = 13.6), 3.79[c] (m, 1H), 4.41[c] (m, 1H), 7.21 (m, 4H). ^{13}C NMR (δ,

75 MHz): 21.2,[c] 27.8, 27.9,[c] 28.7, 28.8,[c] 40.3, 41.2,[c] 41.3,[c] 41.4, 58.1,[c] 58.7, 67.1, 74.8, 76.8, 121.2,[c] 129.8,[c] 129.9, 131.3,[c] 131.5, 132.2, 137.0. IR (neat): 2236 cm^{-1}. HRMS: calcd. for $C_{20}H_{32}SNO_2$ (MH^+) m/z 350.2154, found 350.2138.

***erythro*-1-Phenyl-5-(p-tolylthio)-2,4-pentanediol (*erythro*-12).** A solution of TMSI (0.21 mmol) in CH_2Cl_2 (3 mL) was added to a solution of ***erythro*-10** (0.08 mmol) in CH_2Cl_2 (15 mL) at -20 °C. The mixture was stirred for 15 min and quenched with 5% aqueous $NaHCO_3$, extracted with CH_2Cl_2, and dried over K_2CO_3. Column chromatography (step gradient elution, hexane : ether : CH_2Cl_2 10:1:2, 5:1:2, and 3:1:2) afforded 0.012 g (50%) of ***erythro*-12** and 0.001 g (3%) of ***erythro*-10**. R_f 0.65 (hexane/ether, 5:1). ^1H NMR (δ, 500 MHz): 1.57, 1.76 (2 dt, 2H, $J_1 = J_2 = 10.0$, $J_3 = 14.3$, $J_4 = J_5 = 2.4$), 2.32 (s, 3H), 2.73, 2.78 (2 dd, 2H, $J_1 = 5.8$, $J_2 = 7.2$, $J_5 = 13.5$), 2.86, 2.99 (2 dd, 2H, $J_1 = 4.6$, $J_2 = 8.0$, $J_5 = 13.6$), 3.12, 3.48 (2 s, 2H), 3.85, 4.04 (2 m, 2H), 7.20 (m, 9H). ^{13}C NMR (δ, 83.3 MHz): 21.4, 41.6, 43.0, 44.7, 70.7, 73.6, 126.9, 129.0, 129.9, 130.3, 131.3, 137.4, 138.4. HRMS: calcd. for $C_{18}H_{22}SO_2$ (M^+) m/z 302.1340, found 302.0877.

***threo*-1-Phenyl-5-(p-tolylthio)-2,4-pentanediol (*threo*-12)** was synthesized from ***threo*-10** by the method described for ***erythro*-12**. Yield is 50%. R_f 0.65 (hexane/ether, 5:1). ^1H NMR (δ, 300 MHz): 1.72 (m, 2H), 2.32 (s, 3H), 2.75, 2.89, 3.06 (3 m, 4H), 3.99, 4.15 (m, 2H), 7.25 (m, 9H). ^{13}C NMR (83.3 MHz): 21.4, 41.3, 42.9, 44.5, 67.4, 70.4, 127.0, 129.0, 129.8, 130.3, 131.6, 137.4, 138.5. HRMS: calcd. for $C_{18}H_{22}SO_2$ (M^+) m/z 302.1340, found 302.1162.

Acknowledgment

The authors acknowledge ND EPSCoR (grant No. OSR-9452892), the National Institute of General Medical Sciences (grant No. 1 R15 GM/OD55965-

01), and the University of North Dakota for financial support. Undergraduate Summer Research Assistantships for D.M.W. and J.K. were provided by the NSF-REU program (grant No. CHE-9619804). We would like to thank Danwei Li and Jessica L. Smith for their help in carrying out some of the experiments.

References

1. Smit, W.A.; Caple, R.; Smoliakova, I.P. *Chem. Rev.* **1994**, *94*, 2359.
2. a) Smoliakova, I.P.; Smit, W.A.; Lutzenko, A.I. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1987**, 119; *Chem. Abstr.* **1987**, *107*, 175155j. b) Smoliakova, I.P.; Smit, W.A. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1988**, 2792; *Chem. Abstr.* **1989**, *110*, 231204a. c) Smoliakova, I. P.; Smit, W. A. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1990**, 2036. *Chem. Abstr.* **1990**, *112*, 118356e. d) Smoliakova, I.P.; Smit, W.A.; Bubnov, Yu.N.; Shashkov, A.S. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1991**, 1100; *Chem. Abstr.* **1991**, *115*, 158890t. e) Smoliakova, I.P.; Caple, R.; Magnuson, V.R.; Polyakov, V.R.; Smit, W.A.; Shashkov, A.S. *J. Chem. Soc. Perkin Trans. I* **1995**, 1065. f) Hayford, A.; Lovdahl, M.; Lazareva, M.I.; Kryschenko, Y.K.; Johnson, T.; Dilman, A.D.; Smoliakova, I.P.; Caple, R.; Smit, W.A. *Mendeleev Commun.* **1997**, 48.
3. Lazareva, M.I.; Kryschenko, Y.K.; Caple, R.; Wakefield, D.; Hayford, A.; Smit, W.A.; Shashkov, A.S. *Tetrahedron Lett.* **1998**, *39*, 8787.
4. a) Atkinson, R.S. *Stereoselective Synthesis*; John Wiley & Sons, Inc., Chichester, 1995. b) Ager, D.J.; East, M.B. *Asymmetric Synthetic Methodology*; CPC Press, Inc., Boca Raton, 1996.
5. Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*; 3rd ed., John Wiley & Sons, Inc., New York, 1999.
6. a) Tietze, L.F.; Schuffenhauer, A. *Eur. J. Org. Chem.* **1998**, 1629 and references cited therein. b) Hori, K.; Ito, J.; Ohta, T.; Furukawa, I. *Tetrahedron* **1998**, *54*, 12737. c) Dujardin, G.; Rossignol, S.; Brown, E. *Synthesis* **1998**, 763. d) Desimoni, G.; Gamba, A.; Monticelli, M.; Nicola, M.; Tacconi, G. *J. Am. Chem. Soc.* **1976**, *98*, 2947. e) Lanfermann, H.; Doepp, D. *J. Inf. Rec. Mater.* **1994**, *21*, 545. f) Tietze, L. F.; Hartfiel, U.; Huebsch, T.; Voss, E.; Wichmann, J. *Chem. Ber.* **1991**, *124*, 881.
7. a) Yamaguchi, H.; Doiuchi, T.; Kawamoto, K. *Macromolecules* **1985**, *18*, 2120. b) Ledwith, A.; Lockett, E. *Polymer* **1975**, *16*, 31. Kunitake, T.; Takarabe, K. *Makromol. Chem.* **1981**, *182*, 817. c) Tarvin, R. F.; Aoki, S.; Stille, J.K. *Macromolecules* **1972**, *5*, 663.

8. a) Nedolya, N.A.; Baranskii, V.A.; Trofimov, B.A. *Zh. Org. Khim.* **1995**, *31*, 321. b) Nedolya, N.A.; Trofimov, B.A. *Org. React.* **1978**, *15*, 492. c) Militzer, H.-C.; Schomenauer, S.; Otte, C.; Puls, C.; Hain, J.; Brase, S.; Meijere, A. *Synthesis* **1993**, 998.
9. Fieser, M.; Fieser, L.F.P. *Reagents for Organic Synthesis*, Wiley: New York, 1975, Vol. 5, p. 523.
10. Burgstahler, A.W.; Nordin, Z.C. *J. Am. Chem. Soc.* **1961**, *83*, 198.
11. Dukstra, H.B. *J. Am. Chem. Soc.* **1935**, *57*, 2257.
12. Kaufman, H.C. *Handbook of Organometallic Compounds*, D. Van Nosrtand Co., Princeton, 1961, p. 792.

(Received in the USA 05 December 1999)