Stereoselective Synthesis of Highly Susbstituted Tetrahydrofurans

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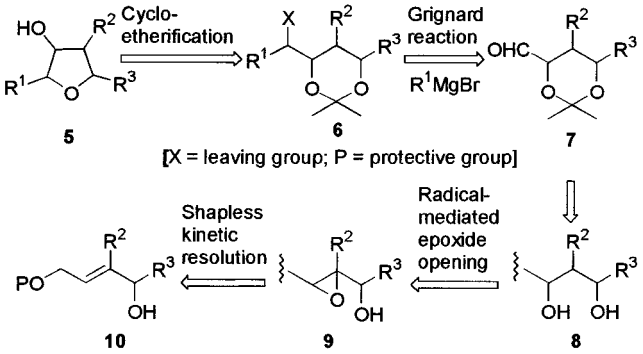
Saturated oxygen heterocycles, essential structural components of large number of organic natural products,[1] are attracting increased attention as organic chemists develop new methodologies for their synthesis.[2] In this paper, we describe an efficient strategy for the synthesis of highly substituted tetrahydofurans[3] **1**−**4** following an acid-catalyzed cycloetherification method. The idea emanated from the known[4] susceptibility of linear molecules having S_N2 active sites to undergo spontaneous ring closure, induced by heteroatoms at the γ-position to produce thermodynamically favorable five-membered cyclic products, a concept exploited by us recently to synthesize furanoid sugar amino acids.[5] The basic strategy followed in our present work for the synthesis of substituted tetrahydrofuran **5** is summarized in Scheme 1. A facile leaving group X in the γ-position of the acyclic precursor **6** is knocked off smoothly under very mild conditions by a suitably positioned oxygen atom in the same molecule giving the tetrahydrofuran framework of **5**. The acyclic precursor **6** was, in turn, prepared from a chiral aldehyde **7** using a diastereoselective Grignard addition reaction. A novel radical-mediated method developed by us recently[6] for the regioselective opening of trisubstituted 2,3-epoxy alcohols **9** at the more substituted 2-position using $cp_2Ti(III)Cl$, and cyclohexa-1,4-diene provided the chiral 1,3-diol **8**, the precursor of **7**. The same method has now been extended here for the first time to open a disubstituted epoxy alcohol also giving exclusively the 1,3-diol that was used for the synthesis of **4**. Sharpless kinetic resolution[7] of the allylic alcohols **10** provided the requisite chiral epoxy alcohols **9**. It was to demonstrate the practical utility of our radical-mediated epoxide opening methodology that we undertook the syntheses of these polysubstituted tetrahydrofuran moieties. The four key reactions—Sharpless kinetic resolution, our radical-mediated regioselective epoxide ring-opening reaction, a diastereoselective Grignard addition reaction, and finally, a facile acid-catalyzed cycloetherification step—outline the essence of our present work.

Scheme 1. General Strategy Followed for the Synthesis of Substituted Tetrahydrofurans 5



Scheme 2 unfolds the details of the route followed for the synthesis of **1**. The starting 1,3-diol **12** was prepared from the allylic alcohol **11** in two steps—Sharpless catalytic kinetic resolution using natural diisopropyl (+)-L-tartrate (85% ee determined by Mosher's ester method) followed by treatment of the resulting epoxy alcohol with cp_2TiCl and cyclohexa-1,4-diene according to the reported procedure.[8] Acetonide protection of the diol using catalytic amount of camphorsulfonic acid (CSA) in CH_2Cl_2 and 2,2-dimethoxypropane and subsequent debenzylation by hydrogenation furnished the intermediate **13** in 92% yield. Oxidation of the primary hydroxyl group using

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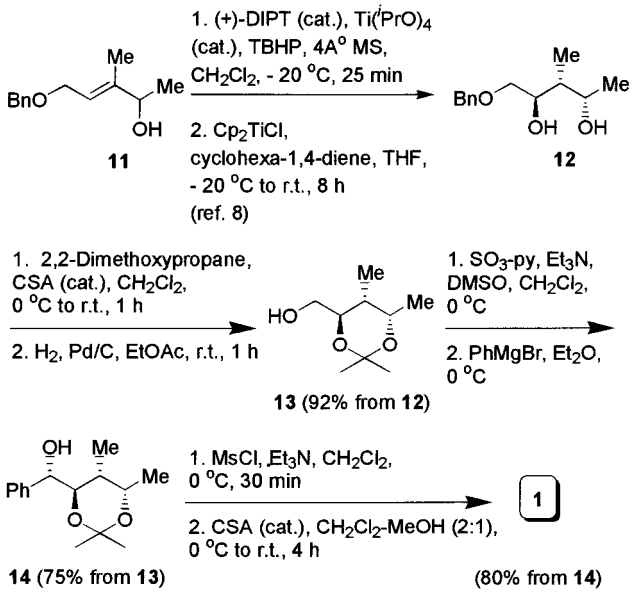
Scheme 2. Stereoselective Synthesis of Compound 1



SO_3−pyridine complex gave an aldehyde, which was treated with PhMgBr to get selectively the anti product **14** with an approximately 4:1 anti/syn ratio in 75% yield from **13**. The isomers could be easily separated by standard silica gel column chromatography. The formation of the anti product as the major diastereomer is consistent with the nonchelate controlled Felkin−Anh model.[9] The PhC*H*(OH) chemical shift of **14** in its D_2O-exchanged ^{1}H NMR spectrum appeared as a doublet at δ 4.51 with a coupling constant of 7 Hz, which is in agreement with the theoretical coupling constants of similar products.[10,11]

Treatment of **14** with methanesulfonyl chloride (MsCl) and Et_3N gave an intermediate mesylate, which was used directly in the next step after aqueous workup without purification. Finally, the crucial cycloetherification reaction was carried out smoothly using a catalytic amount of CSA in CH_2Cl_2−MeOH (2:1) that deprotected the acetonide ring with concomitant ring closure giving the cyclized tetrahydrofuran product **1** in 80% yield from **13**.

The other tetrahydrofurans **2**−**4** were synthesized following the same method as described above in Scheme 2 for the synthesis of **1**. The Sharpless kinetic resolution of the allylic alcohols **10** with catalytic amounts of tartrates (L-tartrate for **2** and **4**; D-tartrate for **3**) gave the requisite chiral epoxy alcohols **9**, with 75% ee for the trisubstituted epoxy alcohols (for **2** and **3**) and 96% ee for the disubstituted compound (for **4**). The Ti(III)-mediated epoxide ring opening gave exclusively the 1,3-diols in excellent yields. In substrates with R^2 = Me, the diastereoselectivity was 5:1 in favor of the expected isomers, (*R*)-Me- (for **2**) and (*S*)-Me-diols (for **3**). In the Grignard addition step (**7** → **6**), the selectivities varied from 2:1 to 4:1 in favor of the anti products. Higher selectivities were observed with bulkier Grignard reagents and in substrates with $R^2 \neq$ H. The purified diastereomers from the Grignard reaction step during the synthesis of **3** were treated separately, after acetonide deprotection, with catalytic amounts of CSA in CH_2Cl_2 and 2,2-dimethoxypropane giving mixtures of five- and six-membered acetonide rings that were separated chromatographically after aqueous workup. The ^{1}H NMR spectrum of the five-membered acetonide from the major anti isomer showed a coupling constant of 7.3 Hz of the vicinal protons C*H*(O)−C*H*(O) of the 1,3-dioxolane ring. The corresponding coupling constant in the five-membered acetonide from the minor syn isomer was 5.6 Hz. These values, which are in conformity with previous literature reports,[12] support the assigned stereochemistry of the products of the Grignard reaction. The two-step cycloetherification process—mesylation followed by treatment with acid—proceeded nicely to give the final tetrahydrofurans **2**−**4** in 65−80% yields.

The relative stereochemistries of two final products **2** and **3** were further confirmed by ^{1}H NOE difference spectroscopic studies. While irradiation of the C2-*H* signal of compound **2** at δ 4.02 enhanced the peaks of C3-*H* and C4-*H*, that of C5-*H* peak at 4.56 ppm showed NOE of C4- and C3-*H* resonances. Similarly, in compound **3**, irradiation of C2-*H* peak at 4.2 ppm caused 2% and 1% enhancements of C3- and C4-*H* signals, respectively and C5-*H* showed NOE with C3- and C4-*H*. The stereochemistries of **1** and **4** were similarly assigned.

It was already shown by us that the Ti(III)-induced ring opening of 2,3-epoxy alcohols can be used to synthesize stereoselectively various diastereomers of the "2-methyl-1,3-diol" stereotriad.[6] Excellent diastereoselectivities were achieved in the nucleophilic addition to the aldehydes **7**. The final cyclization reaction gave single isomer in each of the four cases studied. A combination of these reactions has established an efficient protocol employed here for the stereoselective construction of highly substituted tetrahydrofuran rings that may find useful applications in organic synthesis.

Experimental Section

General Procedures. All reactions were carried out in oven- or flame-dried glassware with magnetic stirring under nitrogen atmosphere using dry, freshly distilled solvents, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates with UV light, I_2, 7% ethanolic phosphomolybdic acid−heat, and 2.5% ethanolic anisaldehyde (with 1% AcOH and 3.3% concentrated H_2SO_4)−heat as developing agents. Silica gel finer than 200 mesh was used for flash column chromatography. Yields refer to chromatographically and spectroscopically homogeneous materials unless otherwise stated. IR spectra were recorded as neat liquids or $CHCl_3$ solutions. NMR spectra were recorded on 400 and 500 MHz spectrometers at room temperature of ~21 °C in $CDCl_3$ using tetramethylsilane as internal standard or the solvent signal as secondary standard, and the chemical shifts are shown in δ scales. Multiplicities of NMR signals are designated as s (singlet), d (doublet), t (triplet), q (quartet), br (broad), m (multiplet, for unresolved lines), etc. ^{13}C NMR spectra were recorded with complete proton decoupling. Mass spectra were obtained under electron impact (EI) and liquid secondary ion mass spectrometric (LSIMS) techniques.

Synthesis of 13. To a solution of **12**[8] (700 mg, 3.13 mmol) in dry CH_2Cl_2 (9 mL), 2,2-dimethoxypropane (0.77 mL, 6.26 mmol), and CSA (7 mg, 0.031 mmol) were added sequentially at 0 °C. After being stirred for 1 h at the same temperature, the reaction

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mixture was quenched with saturated $NaHCO_3$ solution, extracted with EtOAc, washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by column chromatography (SiO_2, 4−10% EtOAc in petroleum ether eluant) afforded the acetonide-protected benzyl ether (785 mg, 95%) as a syrupy liquid. It was dissolved in EtOAc (8 mL), Pd on charcoal (10%, 150 mg) was added and subjected to hydrogenation under atmospheric pressure using a H_2-balloon. After 2 h, the reaction mixture was filtered through a short pad of Celite, and the filter cake was washed with EtOAc. The filtrate and the washings were combined and concentrated in vacuo. Purification by column chromatography (SiO_2, 25−30% EtOAc in petroleum ether eluant) afforded **13** (500 mg, 97%) as a syrupy liquid: R_f = 0.3 (silica gel, 25% EtOAc in petroleum ether); $[\alpha]^{22}_D$ −14.2 (*c* 1.6, $CHCl_3$); IR (neat) ν_{max} 3488, 2992, 2940, 1456, 1376, 1224 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.03 (dq, *J* = 6.8, 5.4 Hz, 1 H), 3.74−3.50 (m, 2 H), 3.42 (dt, *J* = 7.4, 2.8 Hz, 1 H), 2.03 (dd, *J* = 7.6, 5.2 Hz, 1 H), 1.68 (m, 1 H), 1.37 (s, 6 H), 1.10 (d, *J* = 6.8 Hz, 3 H), 0.86 (d, *J* = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 100.47, 75.60, 64.96, 64.18, 35.71, 25.01, 24.02, 16.33, 11.55; MS (EI) *m*/*z* 159 (10) [$M^+ - CH_3$]; HRMS (EI) calcd for $C_8H_{15}O_3$ [$M^+ - CH_3$] 159.1021, found 159.1018.

Synthesis of 14. To an ice-cooled solution of **13** (450 mg, 2.6 mmol) in CH_2Cl_2 (4 mL) and DMSO (5.2 mL) were sequentially added Et_3N (1.8 mL, 13 mmol) and SO_3-py (2.07 gm, 13 mmol). The reaction mixture was stirred at 0 °C for 1 h, quenched with saturated aqueous NH_4Cl solution, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was used directly in the next step without further purification. The crude aldehyde was dissolved in dry ether (10 mL) and cooled to 0 °C, and PhMgBr (0.5 M in ether, 10 mL) was added to it. After being stirred for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc, washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by column chromatography (SiO_2, 7−12% EtOAc in petroleum ether eluant) afforded the anti compound **14** (485 mg, 75%) as the major diastereomer: R_f = 0.65 (silica gel, 25% EtOAc in petroleum ether); $[\alpha]^{22}_D$ 9.8 (*c* 1, $CHCl_3$); IR (neat) ν_{max} 3536, 3440, 2976, 2928, 2888, 1440, 1376, 1224, 1184 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.38−7.30 (m, 5 H), 4.54 (dd, *J* = 6.6, 3.4 Hz, 1 H), 4.09 (dq, *J* = 6.6, 4.8 Hz, 1 H), 3.41 (dd, *J* = 7.4, 6.6 Hz, 1 H), 3.07 (d, *J* = 3.4 Hz, 1 H), 1.77 (m, 1 H), 1.39 and 1.35 (two s, 6 H), 1.05 (d, *J* = 6.6 Hz, 3 H), 0.41 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.04, 128.19, 127.91, 127.23, 100.71, 79.17, 76.34, 65.0, 36.37, 25.31, 23.96, 16.43, 11.40; MS (EI) *m*/*z* 235 (4) [$M^+ - CH_3$]; HRMS (EI) calcd for $C_{14}H_{19}O_3$ [$M^+ - CH_3$] 235.1334, found 235.1329.

Tetrahydrofuran 1. To a solution of **14** (300 mg, 1.2 mmol) in CH_2Cl_2 (5 mL) were sequentially added Et_3N (0.33 mL, 2.4 mmol) and MsCl (0.14 mL, 1.8 mmol) at 0 °C. After being stirred for 0.5 h at the same temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with ether, washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was used directly in the next step without further purification.

To a solution of the crude mesylate in CH_2Cl_2/MeOH (2:1, 6 mL) was added CSA (28 mg, 0.12 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was allowed to come to room temperature slowly and stirred for 2 h. It was then diluted with ether, washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by column chromatography (SiO_2, 10−20% EtOAc in petroleum ether eluant) afforded the tetrahydrofuran **1** (184 mg, 80%) as a syrupy liquid: R_f = 0.5 (silica gel, 25% EtOAc in petroleum ether); $[\alpha]^{22}_D$ −38.8 (*c* 2, $CHCl_3$); IR (neat) ν_{max} 3425, 3000, 2950, 1500, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.4−7.2 (m, 5 H), 4.86 (d, *J* = 5.2 Hz, 1 H), 4.48 (dq, *J* = 7.1, 6.3 Hz, 1 H), 4.21 (q, *J* = 5.2 Hz, 1 H), 2.33 (ddq, *J* = 7.3, 7.1, 5.2 Hz, 1 H), 1.76 (d, *J* = 5.2 Hz, 1 H), 1.29 (d, *J* = 6.3 Hz, 3 H), 1.05 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.01, 128.35, 127.28, 125.37, 84.68, 81.38, 77.50, 40.12, 17.30, 7.62; MS (EI) *m*/*z* 192 (2) [M^+]; HRMS (EI) calcd for $C_{12}H_{16}O_2$ [M^+] 192.1150, found 192.1155.

Tetrahydrofuran 2: R_f = 0.55 (silica gel, 20% EtOAc in petroleum ether); $[\alpha]^{22}_D$ −2.1 (*c* 0.47, $CHCl_3$); IR (neat) ν_{max} 3425, 2950, 2925, 2850, 1100, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.7−7.2 (m, 15 H), 4.56 (d, *J* = 7.3 Hz, 1 H), 4.02 (dt, *J* = 8.8, 3 Hz, 1 H), 3.94−3.83 (m, 2 H), 3.65 (ddd, *J* = 9.4, 7.3, 4.8 Hz, 1 H), 2.03−1.78 (m, 3 H), 1.68 (d, *J* = 4.8 Hz, 1 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 1.07 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.40, 135.59, 134.00, 133.91, 129.57, 129.53, 128.47, 127.63, 127.61, 125.82, 85.43, 84.43, 80.76, 60.65, 47.24, 37.77, 26.88, 19.22, 14.38; MS (LSIMS) *m*/*z* 460 (8) [M^+].

Tetrahydrofuran 3: R_f = 0.45 (silica gel, 25% EtOAc in petroleum ether); $[\alpha]^{22}_D$ 11.5 (*c* 2.7, $CHCl_3$); IR (neat) ν_{max} 3450, 2975, 2950, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.7−7.3 (m, 10 H), 4.21 (ddd, *J* = 9.2, 5.7, 4.7 Hz, 1 H), 3.91 (dd, *J* = 6.1, 4.7 Hz, 1 H), 3.84 (dq, *J* = 6.4, 4.7 Hz, 1 H), 3.78 (dd, *J* = 7.4, 5.7 Hz, 2 H), 2.29 (ddq, *J* = 7.4, 6.1, 4.7 Hz, 1 H), 1.82−1.65 (two m, 2 H), 1.56 (br s, 1 H), 1.23 (d, *J* = 6.4 Hz, 3 H), 1.04 (s, 9 H), 0.95 (d, *J* = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.57, 135.55, 134.00, 133.91, 129.50, 129.49, 127.57, 127.55, 80.09, 78.72, 76.80, 61.30, 40.05, 34.14, 26.86, 19.63, 19.18, 7.67; MS (LSIMS) *m*/*z* 399 (40) [M^+ + H], 421 (20) [M^+ + Na]; HRMS (LSIMS) calcd for $C_{24}H_{35}O_3Si$ [M^+ + H] 399.2355, found 399.2348.

Tetrahydrofuran 4: R_f = 0.5 (silica gel, 25% EtOAc in petroleum ether); $[\alpha]^{22}_D$ 30.4 (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3418, 2924, 1453, 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47−7.24 (m, 10 H), 5.36 (dd, *J* = 7.6, 7.2 Hz, 1 H), 5.03 (d, *J* = 5.1 Hz, 1 H), 4.41 (ddt, *J* = 6.6, 5.7, 5.1 Hz, 1 H), 2.73 (ddd, *J* = 12.9, 7.2, 6.6 Hz, 1 H), 2.14 (ddd, *J* = 12.9, 7.6, 6.6 Hz, 1 H), 1.81 (d, *J* = 5.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.17, 140.69, 128.53, 127.70, 127.45, 125.59, 125.53, 86.94, 79.37, 79.30, 42.75; MS (LSIMS) *m*/*z* 239 (12) [M^+ − H]; HRMS (LSIMS) calcd for $C_{16}H_{16}O_2$ [M^+] 240.1150, found 240.1151.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **1**−**4**. This material is available via the Internet at http://pubs.acs.org.

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