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ENANTIOSELECTIVE SYNTHESIS OF 1-VINYL-1,2-DIOLS, VINYL EPOXIDES AND α,β-DIALKOXY ALDEHYDES

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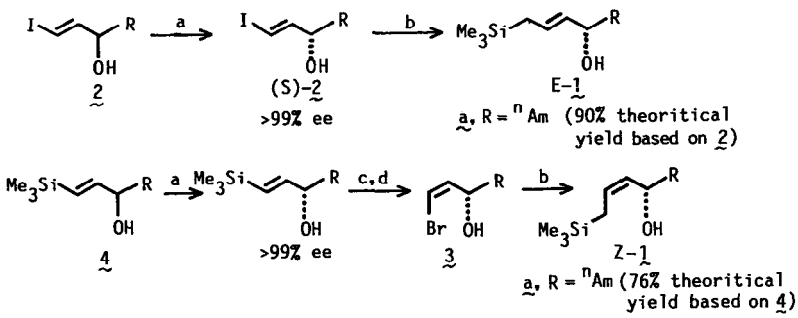
Summary: A practical synthetic method of chiral γ-trimethylsilylmethyl allylic alcohols (1) with both E- and Z-configuration has been developed. The alcohols 1 are readily converted into 1-vinyl-1,2-diols (5) via diastereoselective epoxidation followed by the reaction with $^{n}Bu_4NF$. The conversion of 1 into vinyl epoxides or α,β-dialkoxy aldehydes is also carried out.

Enantioselective synthesis of functionalized 1,2-diols has been attracted much interest in recent years, because many natural products of current interest contain 1,2-diol substructure, and in addition 1,2-diols are recognized as valuable intermediates for use in a variety of synthetic transformations.[1,2] In the present paper, we report a new efficient method for the synthesis of functionalized chiral 1,2-diols, i.e., 1-vinyl-1,2-diols, and their conversion into vinyl epoxides and α,β-dialkoxy aldehydes.

Recently, we have reported a practical method for the synthesis of chiral (E)-allylic alcohols having CH_2SiMe_3 group at γ-position (E-1) by the procedure shown in Scheme 1.[3] We have now succeeded in synthesizing Z-isomer of 1 by

Scheme 1.



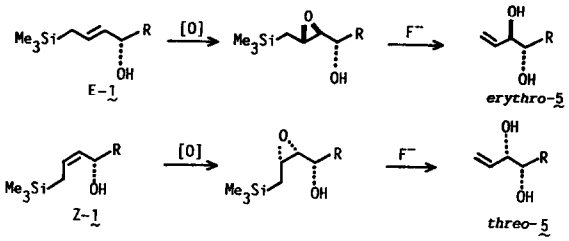
(a) $^{t}BuOOH$ (TBHP), $Ti(O^{i}Pr)_4$, D-(-)-diisopropyl tartrate (D-(-)-DIPT), CH_2Cl_2; (b) Me_3SiCH_2MgCl (2.2 equiv), cat. $Ni(dppp)Cl_2$, Et_2O, r.t.; (c) Br_2, CH_2Cl_2, -20 °C; (d) $^{n}Bu_4NF$, THF, 0 °C.

the similar method. Thus, Z-1a was obtained by the Ni-catalyzed coupling reaction of (Z,S)-γ-bromo allylic alcohol (3a) with Me_3SiCH_2MgCl,[4,5] the former of which can be readily obtained in chiral form from racemic (E)-γ-trimethylsilyl allylic alcohol (4a) by using the Sharpless kinetic resolution reaction[6,7] as a key step (Scheme 1).

With the compound 1, we have reasoned that E-1 could allow a good entry to the erythro-1,2-diols (erythro-5) and Z-1 to the threo-5, via diastereo-

selective epoxidation followed by treatment of the resulting epoxy alcohols with $^{n}Bu_4NF$ (Scheme 2), since, thanks to the extensive studies, it is possible

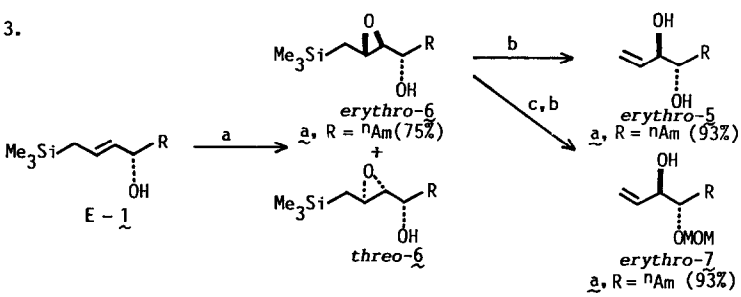
Scheme 2.



to carry out the highly diastereoselective epoxidation of secondary allylic alcohols by using the following three reagents properly, 1) organic per-acids,[8] 2) $VO(acac)_2$ / TBHP,[8b-d,9] and 3) [Ti(L- or D-DIPT)$(O^{i}Pr)_2]_2$ / TBHP.[7]

The epoxidation of E-1a using $Ti(O^{i}Pr)_4$ (0.20 equiv) - L-DIPT (0.24 equiv.) - TBHP (2.0 equiv) in the presence of molecular sieves 4A in CH_2Cl_2 (-20 °C, 20 h) was found to give the highest selectivity to afford the erythro-, and threo-epoxy alcohol 6a in a ratio of 9 : 1 which were readily separated by column chromatography on silica gel (Rf value: erythro-6a; 0.48, and threo-6a; 0.39 / hexane/Et_2O = 3/1). The isolated yield of erythro-6a[10] ($[\alpha]_D^{25}$ +6.7° (c 0.99, $CHCl_3$)) was 75% based on E-1a. Treatment of erythro-6a thus obtained with $^{n}Bu_4NF$[11] in THF (0 °C, 0.5 h) directly or after protection of the hydroxy group as methoxymethyl ether provided erythro-5a[10] ($[\alpha]_D^{25}$ +2.6° (0.93, $CHCl_3$)) in 93% yield or its monomethoxymethyl ether 7a[10,12] ($[\alpha]_D^{25}$ +48.0° (c 1.30, $CHCl_3$)) in 93% yield, respectively (Scheme 3).

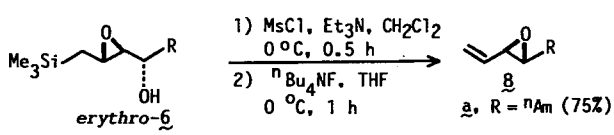
Scheme 3.



(a) TBHP (2.0 equiv), $Ti(O^{i}Pr)_4$ (0.20 equiv), L-(+)-DIPT (0.24 equiv), CH_2Cl_2, -20 °C, 20 h; (b) $^{n}Bu_4NF$, THF, 0 °C, 0.5 h; (c) MOMCl, Et_3N, CH_2Cl_2, r.t., 16 h.

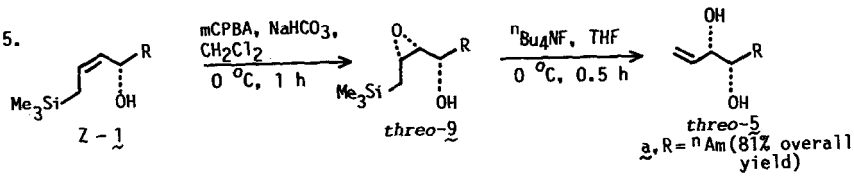
From 5 or 7, it is possible to prepare the chiral vinyl epoxides 8 which are also recognized as important synthetic intermediates. However, the epoxide 8 was found to be obtained directly from 6. Thus, mesylation of erythro-6a (MsCl, Et_3N, CH_2Cl_2, 0 °C, 0.5 h) followed by treatment of the resulting mesylate with $^{n}Bu_4NF$ in THF (0 °C, 1 h) afforded 8a[10,13] ($[\alpha]_D^{25}$ +23.0° (c 1.25, $CHCl_3$)) in 75% overall yield (Scheme 4).

Scheme 4.



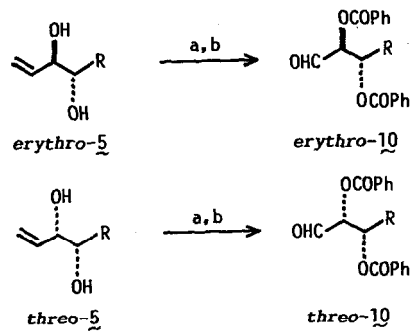
Highly diastereoselective epoxidation of Z-1 to threo-9 was found to be readily carried out by using mCPBA. Epoxidation of Z-1a with slightly excess of mCPBA in the presence of $NaHCO_3$ in CH_2Cl_2 (0 °C, 1 h) furnished threo-9a as a sole diastereoisomer and about 5% of the threo-5a; from this reaction mixture, threo-5a,[10] ($[\alpha]_D^{25}$ -23.3° (c 1.04, $CHCl_3$)) was obtained in 81% yield (based on Z-1a) by treatment with $^nBu_4NF$ (Scheme 5).

Scheme 5.



We also carried out the conversion of 5 into the α,β-dialkoxy aldehydes 10 via ozonolysis after conversion into the corresponding dibenzoates (Scheme 6), since the enantioselective synthesis of which has been attracted much interest in relation to the synthesis of metabolites of arachidonic acid such as lipoxin A, lipoxin B and punaglandin.[2] The yield and $[\alpha]_D$ values of 10 are as follows: erythro-10a[10]; 61% yield, $[\alpha]_D^{25}$ -22.7° (c 1.05, $CHCl_3$), lit.[2g] $[\alpha]_D^{25}$ -23.0° (c 1.13, $CHCl_3$), threo-10a[10]; 58% yield, $[\alpha]_D^{25}$ -70.5° (c 0.82, $CHCl_3$), lit.[2g] $[\alpha]_D^{25}$ -69.1° (c 2.07, $CHCl_3$).

Scheme 6.



(a) PhCOCl, pyridine, r.t.; (b) O_3, MeOH, -78 °C then Me_2S.

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4) The coupling reaction was carried out as follows: to a solution of 3a (795 mg, 3.84 mmol) in Et_2O (2 ml) was added Me_3SiCH_2MgCl (5.45 ml, 8.45 mmol, 1.50 M in Et_2O) at 0°C. After 10 min, Ni(dppp)Cl_2 (62.4 mg, 0.12 mmol) was added and the resulting solution was stirred at r.t. for 3 h. Usual work up followed by chromatography on silica gel gave Z-1a (690 mg, 84%). Similarly (S)-2a (31.3 g, 123 mmol) was coupled with Me_3SiCH_2MgCl (177 ml, 274 mmol, 1.55 M in Et_2O) in the presence of Ni(dppp)Cl_2 (667 mg, 1.23 mmol) to provide E-1a (26.3g, 100%). Z-1a: ^{1}H NMR (CCl_4) δ 0.07 (s, 9H), 0.91 (t, J = 6.0 Hz, 3H), 1.10-1.76 (m, 8H), 1.52 (d, J = 7.5 Hz, 2H), 2.16 (br s, 1H), 4.03-4.37 (m, 1H), 5.05-5.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 130.8, 128.1, 67.3, 37.6, 31.9, 25.1, 22.6, 19.0, 13.9, -1.8; $[\alpha]_D^{25}$ -12.3° (c 1.01, $CHCl_3$). E-1a: ^{1}H NMR (CCl_4) δ 0.04 (s, 9H), 0.90 (t, J = 5.4 Hz, 3H), 1.08-1.60 (m, 8H), 1.42 (d, J = 8.4 Hz, 2H), 2.85 (br s, 1H), 3.72-4.00 (m, 1H), 5.17 (dd, J = 7.0, 16.6 Hz, 1H), 5.49 (dt, J = 16.6, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 131.9, 128.6, 73.6, 37.5, 31.9, 25.3, 22.8, 22.6, 14.0, -2.0; $[\alpha]_D^{25}$ -23.3° (c 0.92, $CHCl_3$).

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10) erythro-5a: ^{1}H NMR (CCl_4, D_2O) δ 0.86 (t, J = 5.6 Hz, 3H), 1.03-1.65 (m, 8H), 3.38-3.66 (m, 1H), 3.95 (dd, J = 3.0, 6.6 Hz, 1H), 4.98-5.30 (m, 2H), 5.77 (ddd, J = 6.6, 10.8, 18,0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 136.2, 116.9, 75.9, 74.2, 31.7, 25.5, 22.4, 13.8. erythro-6a: ^{1}H NMR (CCl_4, D_2O) δ 0.11 (s, 9H), 0.54-1.88 (m, 13H), 2.50 (dd, J = 2.4, 3.6 Hz, 1H), 2.93 (ddd, J = 2.4, 6.0, 8.4 Hz, 1H), 3.36-3.69 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 69.0, 62.6, 53.4, 33.7, 31.8, 25.2, 22.5, 20.5, 13.9, -1.2. erythro-7a: ^{1}H NMR ($CDCl_3$, D_2O) δ 0.89 (t, J = 6.0 Hz, 3H), 1.02-1.70 (m, 8H), 3.42 (s, 3H), 3.40-3.70 (m, 1H), 3.96-4.20 (m, 2H), 5.12-5.48 (m, 2H), 5.91 (ddd, J = 5.7, 10.1, 17.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 136.6, 115.9, 97.1, 83.5, 74.2, 55.5, 31.6, 30.6, 25.3, 22.3, 13.7. 8a: ^{1}H NMR (CCl_4) δ 0.87 (t, J = 6.0 Hz, 3H), 1.03-1.81 (m, 8H), 2.47-2.68 (m, 1H), 2.82 (dd, J = 2.2, 6.6 Hz, 1H), 4.92-5.16 and 5.25-5.36 (m, 2H), 5.46 (ddd, J = 6.6, 9.6, 18.0 Hz 1H); ^{13}C NMR ($CDCl_3$) δ 136.0, 118.5, 60.5, 58.6, 32.0, 31.6, 25.6, 22.5, 13.9. threo-5a: ^{1}H NMR (CCl_4, D_2O) δ 0.87 (t, J = 6.0 Hz, 3H), 1.00-1.82 (m, 8H), 3.10-3.41 (m, 1H), 3.70 (t, J = 6.8 Hz, 1H), 4.93-5.33 (m, 2H), 5.70 (ddd, J = 6.8, 10.8, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 137.8, 117.0, 76.2, 74.4, 32.8, 31.8, 25.2, 22.5, 13.9. erythro-10a: ^{1}H NMR (CCl_4) δ 0.88 (t, J = 6.0 Hz, 3H), 1.13-2.23 (m, 8H), 5.34 (dd, J = 1.2, 3.0 Hz, 1H), 5.51-5.75 (m, 1H), 7.20-8.14 (m, 10H), 9.63 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 195.9, 165.6, 165.5, 133.6, 133.2, 129.8, 129.6, 128.7, 128.5, 128.4, 79.0, 72.8, 31.3, 30.2, 25.0, 22.3, 13.8. threo-10a: ^{1}H NMR (CCl_4) δ 0.85 (t, J = 5.6 Hz, 3H), 1.03-2.06 (m, 8H), 5.40 (d, J = 3.6 Hz, 1H), 5.63 (dt, J = 3.6, 6.6 Hz, 1H), 7.13-8.20 (m, 10H), 9.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 195.3, 165.7, 133.6, 133.3, 129.9, 129.6, 129.4, 128.8, 128.5, 128.4, 78.7, 71.7, 31.3, 30.7, 24.8, 22.3, 13.8.

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12) The optical purity was confirmed to be >99% ee by ^{1}H NMR analysis of the derived MTPA ester.

13) The optical purity and absolute configuration were confirmed by conversion into 2(R),3(R)-epoxy-1-octanol ($[\alpha]_D^{25}$ +43.1° (c 0.57, $CHCl_3$; lit[14] for 2(S),3(S)-epoxy-1-octanol, $[\alpha]_D$ -44° (c 1.0, $CHCl_3$)) via ozonolysis followed by reduction with $NaBH_4$ in MeOH.

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