Synthesis of isoprene atmospheric oxidation products: isomeric epoxydiols and the rearrangement products *cis-* and *trans-*3-methyl-3,4-dihydroxytetrahydrofuran

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Figure S1. $^1$H NMR (400 MHz, CDCl$_3$) of erythro- and threo-1-(2-methylloxiran-2-yl)ethane-1,2-diol (IEPOX-1). The signal for the epoxy ring proton cis to the methine hydroxy group (3$'$H$_b$) in erythro isomer is shifted significantly downfield relative to that of the threo isomer, in accord with the observation for structural analogs [Adam, J. Am. Chem. Soc. 1993, 115, 7226.]. The assignment of the erythro diastereomer as the major product is consistent with the assignment based on the $^{13}$C chemical shifts (see $^{13}$C NMR, Figure S2).
Figure S2. $^{13}$C NMR (100 MHz, CDCl$_3$) of erythro- and threo-1-(2-methyloxiran-2-yl)ethane-1,2-diol (IEPOX-1). The distinction between threo and erythro diastereomers is based on the observation that the chemical shift of all oxygen-bearing carbon atoms of the erythro diastereomers are 0.1-3.4 ppm upfield relative to those of the corresponding threo diastereomers [Adam JOC 1997]. Of the two sets of signals, the set having upfield chemical shifts for all oxygen-bearing carbons is consequently assigned to the erythro diastereomer, which is the major product, and the second set is assigned to the minor threo diastereomer.
Figure S3. $^1$H NMR (400 MHz, CDCl$_3$) of 2-(oxiran-2-yl)propane-1,2-diol (IEPOX-2). Assignments of signals to erythro and threo diastereomers is tentative based on the NMR spectrum of the close structural analog linalool epoxide for which the absolute stereochemistry has been established. [a]. Morales, C. P.; Catalan, J.; Domingo, V.; Delgado, J. A. G.; Dobado, J. A.; Herrador, M. M.; del Moral, J. F. Q.; Barrero, A. F. J. Org. Chem. 2011, 76, 2494. b). Khomenko, T.M.; Tatarova, L. E.; Korchagina, D. V.; Barkhash, V. A.. Russ. J. Org. Chem. 2002, 38, 4983].
Figure S4. $^1$H NMR (400 MHz, CDCl$_3$) of (Z)-2-methylbut-2-ene-1,4-diol (8).
Figure S5. $^1$H NMR (400 MHz, CDCl$_3$) of cis-2-methyl-2,3-epoxybutane-1,4-diol (IEPOX-3).
Figure S6. $^{13}$C NMR (100 MHz, CDCl$_3$) of cis-(2-methyloxirane-2,3-diyl)dimethanol (IEPOX-3).
**Figure S7.** $^1$H NMR (400 MHz, D$_2$O) of *cis*-2-methyl-2,3-epoxybutane-1,4-diol (IEPOX-3).
Figure S8. $^1$H and NOESY 1D NMR (400 MHz, D$_2$O) of cis-2-methyl-2,3-epoxybutane-1,4-diol (IEPOX-3). The cis geometry of IEPOX-3 is confirmed by strong dipolar coupling between the methyl group and the oxirane proton H3 the 1D NOESY spectrum.
Figure S9. $^1$H NMR (400 MHz, CDCl$_3$) of trans-4-((tert-butyldimethylsilyl)oxy)-2-methyl-2-buten-1-ol (11).
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$) of (3-(((tert-butyldimethylsilyl)oxy)methyl)-2-methyloxiran-2-yl)methanol (12).
Figure S11. $^1$H NMR (400 MHz, CDCl$_3$) of *trans*-2-methyl-2,3-epoxybutane-1,4-diol (IEPOX-4).
Figure S12. $^{13}$C NMR (100 MHz, CDCl$_3$) of trans-2-methyl-2,3-epoxybutane-1,4-diol (IEPOX-4).
Figure S13. $^1$H NMR (400 MHz, $D_2O$) of trans-2-methyl-2,3-epoxybutane-1,4-diol (IEPOX-4).
Figure S14. $^1$H and NOESY 1D NMR (400 MHz, D$_2$O) of trans-2-methyl-2,3-epoxybutane-1,4-diol (IEPOX-4). The trans-configuration is confirmed by the absence of an NOE correlation between the methyl group and oxirane proton H3 in the 1D NOESY spectrum.
Figure S15. $^1$H NMR (400 MHz, CDCl$_3$) of 4-(benzyloxy)tetrahydrofuran-3-ol (17).
Figure S16. $^{13}$C NMR (100 MHz, CDCl$_3$) of 4-(benzyloxy)tetrahydrofuran-3-ol (17).
Figure S17. $^1$H NMR (400 MHz, CDCl$_3$) of 4-(benzylxyloxy)dihydrofuran-3(2H)-one (18).
Figure S18. $^{13}$C NMR (100 MHz, CDCl$_3$) of 4-(benzyloxy)dihydrofuran-3(2H)-one (18).
Figure S19. $^1$H NMR (400 MHz, CDCl$_3$) of cis-3-methyltetrahydrofuran-3,4-diol (14).
Figure S20. $^{13}$C NMR (100 MHz, CDCl$_3$) of cis-3-methyltetrahydrofuran-3,4-diol (14).
Figure S21. $^1$H and NOESY 1D NMR (400 MHz, CDCl$_3$) of cis-3-methyltetrahydrofuran-3,4-diol (14). In the 1D NOESY spectrum, strong enhancement of the signal for carbinyl H4 on irradiation of the neighboring 3-methyl signal confirms the cis-isomeric structure.
Figure S22. $^1$H NMR (400 MHz, D$_2$O) of trans-3-methyltetrahydrofuran-3,4-diol (15).
Figure S23. $^{13}$C NMR (100 MHz, CDCl$_3$) of trans-3-methyltetrahydrofuran-3,4-diol (15).
Figure S24. $^1$H and NOESY 1D NMR (400 MHz, D$_2$O) of *trans*-3-methyltetrahydrofuran-3,4-diol (15). In contrast to the *cis*-isomer, irradiation of the methyl signal produces a much smaller enhancement of the H4 signal in the 1D NOESY spectrum (see Figure S21).
Figure S25. Positive GC-EIMS of $cis$-3-methyltetrahydrofuran-3,4-diol (14) and $trans$-3-methyltetrahydrofuran-3,4-diol (15).
Figure S26. TIC from analysis of IEPOX isomers, 100 ng/μL in EtOAc: (A) and (B) freshly prepared IEPOX-3 and IEPOX-1, respectively; (C) and (D) the same solutions stored at -20 °C for 1 year.
Figure S27. TIC from solutions of *trans*- and *cis*-MeTHF-3,4-diols, respectively, 100 ng/μL in ETOAc: (A) and (B) freshly prepared *trans*- and *cis*-MeTHF-3,4-diols, respectively; (C) and (D) the same solutions stored at -20 °C for 1 year.