Assessing Potential Oligomerization Reaction Mechanisms of Isoprene Epoxydiols on Secondary Organic Aerosol

Santino J. Stropoli, Corina R. Miner, Daniel R. Hill and Matthew J. Elrod*

Department of Chemistry and Biochemistry, Oberlin College, Oberlin, Ohio, 44074 USA

Email: mjelrod@oberlin.edu

Contents: Bulk solution conditions, NMR assignments, and NMR chemical shift differences

(13 pages, 12 tables, 13 figures)

Bulk solution conditions S-3
Table S1: Solution composition of *cis*-2,3-epoxybutane + methanol reaction S-3
Table S2: Solution composition of *cis*-2,3-epoxybutane + ethylene glycol reaction S-3
Table S3: Solution composition of *cis*-2,3-epoxybutane + glycerol reaction S-3
Table S4: Solution composition of *cis*-2,3-epoxybutane + 2,3-butanediol reaction S-4
Table S5: Solution composition of *cis*-2,3-epoxybutane + *meso*-erythritol reaction S-4
Table S6: Solution composition of *cis*-2,3-epoxybutane + 2-methyltetrol reaction S-4
Table S7: Solution composition of *cis*-2,3-epoxy-1,4-butanediol + methanol reaction S-5
Table S8: Solution composition of *cis*-2,3-epoxy-1,4-butanediol + *meso*-erythritol reaction .. S-5
Table S9: Solution composition of *trans*-β-IEPOX + methanol reaction S-5
Table S10: Solution composition of *trans*-β-IEPOX + ethanol reaction S-6
Table S11: Solution composition of *trans*-β-IEPOX + ethylene glycol reaction S-6
Table S12: Solution composition of *trans*-β-IEPOX + 2-methyltetrol reaction S-6
NMR assignments S-7
Figure S1: *Cis*-2,3-epoxybutane + methanol reaction NMR assignments in D_2O S-7
Figure S2: *Cis*-2,3-epoxybutane + ethylene glycol reaction NMR assignments in D_2O S-8
Figure S3: *Cis*-2,3-epoxybutane + 2,3-butanediol reaction NMR assignments in D_2O S-8
Figure S4: *Cis*-2,3-epoxybutane + *meso*-erythritol reaction NMR assignments in D_2O S-9
Figure S5: *Cis*-2,3-epoxybutane + 2-methyltetrol reaction NMR assignments in D_2O S-9
Figure S6: *Cis*-2,3-epoxy-1,4-butanediol + methanol reaction NMR assignments in D_2O S-9

Figure S7: *Cis*-2,3-epoxy-1,4-butanediol + *meso*-erythritol reaction NMR assignments in D_2O S-10

Figure S8: *Trans*-β-IEPOX + methanol reaction ^1H NMR and ^{13}C NMR assignments in D_2O S-10

Figure S9: *Trans*-β-IEPOX + ethanol reaction ^1H NMR and ^{13}C NMR in ethanol-d_6 ..... S-10

Figure S10: *Trans*-β-IEPOX + ethylene glycol reaction NMR assignments in D_2O S-11

NMR chemical shift differences S-12

Figure S11: Differences in ^{13}C NMR chemical shift between nucleophiles and the *cis*-2,3-epoxybutane hydrolysis product (*racemic* 2,3-butanediol) and corresponding nucleophilic addition products for *cis*-2,3-epoxybutane systems. S-12

Figure S12: Differences in ^{13}C NMR chemical shift between nucleophiles and the *cis*-2,3-epoxy-1,4-butanediol hydrolysis product (*meso*-erythritol) and corresponding nucleophilic addition products for *cis*-2,3-epoxy-1,4-butanediol systems. S-12

Figure S13: Differences in ^{13}C NMR chemical shift between nucleophiles and the *trans*-β-IEPOX hydrolysis product (2-methylerythritol) and corresponding nucleophilic addition products for *trans*-β-IEPOX systems.. ..... S-13

References S-13

Bulk Solution Conditions

	Epoxide	Nucleophile	Acid	Solvent
Volume (µL)	50 µL *cis*-2,3-epoxybutane	232 µL methanol	93 µL 0.20 M TFA (in D_2O)	(neat)
Concentration (M)	1.5 M	15.3 M	0.050 M	

Table S1. Solution composition of *cis*-2,3-epoxybutane + methanol reaction. Concentrations reflect "neat" reaction composition, prior to being combined with D_2O solvent. At this TFA concentration, the lifetime (τ) of a similar *trans*-2,3-epoxybutane nucleophilic addition reaction with water is 100 s.[1]

	Epoxide	Nucleophile	Acid	Solvent
Volume	50 µL *cis*-2,3-epoxybutane	320 µL ethylene glycol	30 µL 0.62 M TFA (in D_2O)	(neat)
Concentration	1.4 M	14.3 M	0.047 M	

Table S2. Solution composition of *cis*-2,3-epoxybutane + ethylene glycol reaction. Concentrations reflect "neat" reaction composition, prior to being combined with D_2O solvent.

	Epoxide	Nucleophile	Acid	Solvent
Volume/Mass	25 µL *cis*-2,3-epoxybutane	0.2644 g glycerol	141 µL 0.13 M TFA (in D_2O)	(neat)
Concentration	0.76 M	7.62 M	0.049 M	

Table S3. Solution composition of *cis*-2,3-epoxybutane + glycerol reaction. Concentrations reflect "neat" reaction composition, prior to being combined with D_2O solvent.

	Epoxide	Nucleophile	Acid	Solvent
Volume	25 µL *cis*-2,3-epoxybutane	255 µL 2,3-butanediol	89 µL 0.20 M TFA (in D_2O)	(neat)
Concentration	0.78 M	7.57 M	0.048 M	

Table S4. Solution composition of *cis*-2,3-epoxybutane + 2,3-butanediol reaction.
Concentrations reflect "neat" reaction composition, prior to being combined with D_2O solvent.

	Epoxide	Nucleophile	Acid	Solvent
Volume/Mass	25 µL *cis*-2,3-epoxybutane	0.3500 g *meso*-erythritol	107 µL 0.375 M TFA (in D_2O)	618 µL D_2O
Concentration	0.38 M	3.821 M	0.053 M	

Table S5. Solution composition of *cis*-2,3-epoxybutane + *meso*-erythritol reaction.

	Epoxide	Nucleophile	Acid	Solvent
Volume/Mass	20 µL *cis*-2,3-epoxybutane	0.3390 g 2-methyltetrol	30 µL 13.2 M TFA	400 µL CD_3OD
Concentration	0.29 M	3.204 M	0.51 M	

Table S6. Solution composition of *cis*-2,3-epoxybutane + 2-methyltetrol reaction.

	Epoxide	Nucleophile	Acid	Solvent
Volume/Mass	0.0104 g *cis*-2,3-epoxy-1,4-butanediol	107 µL CD_3-OD	100 µL 0.375 TFA (in D_2O)	534 µL D_2O
Concentration	0.1348 M	3.55 M	0.051 M	

Table S7. Solution composition of *cis*-2,3-epoxy-1,4-butanediol + methanol reaction. At this TFA concentration, the lifetime (τ) of a similar *cis*-2,3-epoxy-1,4-butanediol nucleophilic addition reaction with water is 3.9 hr.[2]

	Epoxide	Nucleophile	Acid	Solvent
Volume/Mass	0.0105 g *cis*-2,3-epoxy-1,4-butanediol	0.2394 g *meso*-erythritol	100 µL 0.375 M TFA (in D_2O)	476 µL D_2O
Concentration	0.1211 M	3.412 M	0.045 M	

Table S8. Solution composition of *cis*-2,3-epoxy-1,4-butanediol + *meso*-erythritol reaction

	Epoxide	Nucleophile	Acid	Solvent
Volume	10 µL *trans*-β-IEPOX	(solvent)	100 µL 0.375 TFA (in CD_3OD)	640 µL CD_3-OD
Concentration	0.14 M		0.050 M	

Table S9. **Solution composition of *trans*-β-IEPOX + methanol reaction.** At this TFA concentration, the lifetime (τ) of a similar *trans*-β-IEPOX nucleophilic addition reaction with water is 560 s.[2]

	Epoxide	Nucleophile	Acid	Solvent
Volume	10 µL *trans*-β-IEPOX	(solvent)	100 µL 0.375 M TFA (in ethanol-d_6)	640 µL ethanol-d_6
Concentration	0.14 M		0.050 M	

Table S10. Solution composition of *trans*-β-IEPOX + ethanol reaction.

	Epoxide	Nucleophile	Acid/Solvent
Volume	50 µL *trans*-β-IEPOX	300 µL ethylene glycol	1 mL 0.11 M $DCLO_4$ (in D_2O)
Concentration	0.38 M	3.97 M	0.081 M $DCLO_4$

Table S11. Solution composition of *trans*-β-IEPOX + ethylene glycol reaction.

	Epoxide	Nucleophile	Acid	Solvent
Volume/Mass	23 µL *trans*-β-IEPOX	0.3210 g 2-methyltetrol	14 µL 13.1 M TFA	400 µL CD_3OD
Concentration	0.30 M	3.062 M	0.24 M	

Table S12. Solution composition of *trans*-β-IEPOX + 2-methyltetrol reaction.

NMR Assignments

NMR assignments are given for each system in the following sections, along with NMR referencing information. Species are primarily assigned using ^{13}C NMR, as ^{1}H NMR spectra were often uninterpretable due to chemical shift overlap between dimer addition products and nucleophile reactants. Further structural interpretation was mainly achieved using ^{13}C DEPT, while HSQC and HMBC were only used in some cases to confirm assignments, as ^{1}H NMR overlap complicated these spectra as well.

^{1}H NMR assignments are given in black, while ^{13}C NMR assignments are given in blue. Because of prominent chemical shift overlap (primarily due to the presence of excess nucleophile post-reaction), some of the more complex systems could only be partially assigned. Thus, in order to report these assignments, further notation was established and is clarified here. Missing ^{1}H or ^{13}C assignments indicate that the corresponding peaks could not be identified either due to chemical shift overlap or, in the case of deuterated nucleophiles, were too weak in signal due to deuterium splitting. Red text is used for ^{13}C NMR assignments that are speculative, either because it was unclear whether the corresponding peaks were artifacts or because there was insufficient evidence to definitively make an assignment. In addition, double-headed arrows pointing to two separate assignments indicate that the exchanged assignment may instead be correct (often a result of ambiguity in whether the signal originated from the epoxide or nucleophile side of the addition product). Finally, because epoxides were not present post-reaction and thus not observed in NMR spectra, reported epoxide NMR assignments are not specific to each solvent system. Instead, for each set of reported chemical shifts, epoxide NMR assignments correspond to dilute solutions of epoxide in D_2O (calibrated to DSS at 0.0 ppm).

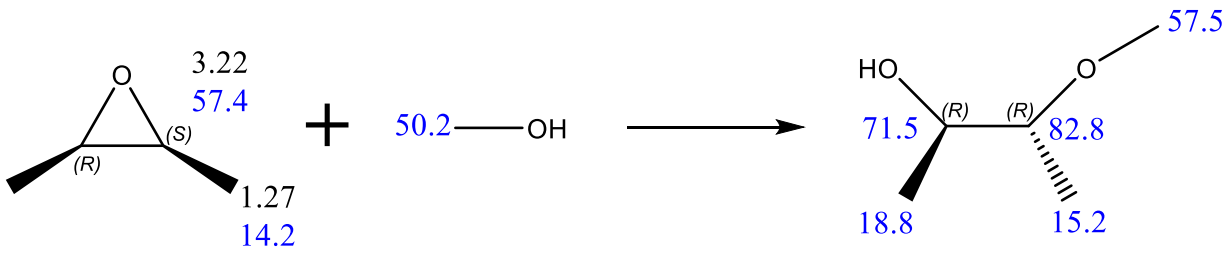

Figure S1. *Cis*-2,3-epoxybutane + methanol reaction NMR assignments in D_2O, referenced to secondary calibration of RR/SS (*racemic*) 2,3-butanediol methyl group at 18.98 ppm. Primary calibration is to *meso*-erythritol at 63.8 ppm.

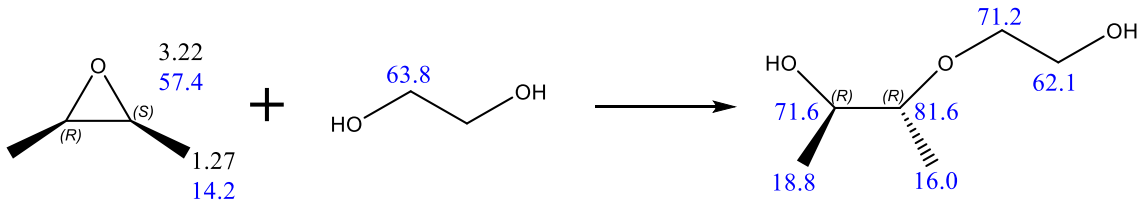

Figure S2. ***Cis*-2,3-epoxybutane + ethylene glycol reaction NMR assignments in D_2O**, referenced to secondary calibration of *racemic* 2,3-butanediol methyl group at 18.98 ppm.

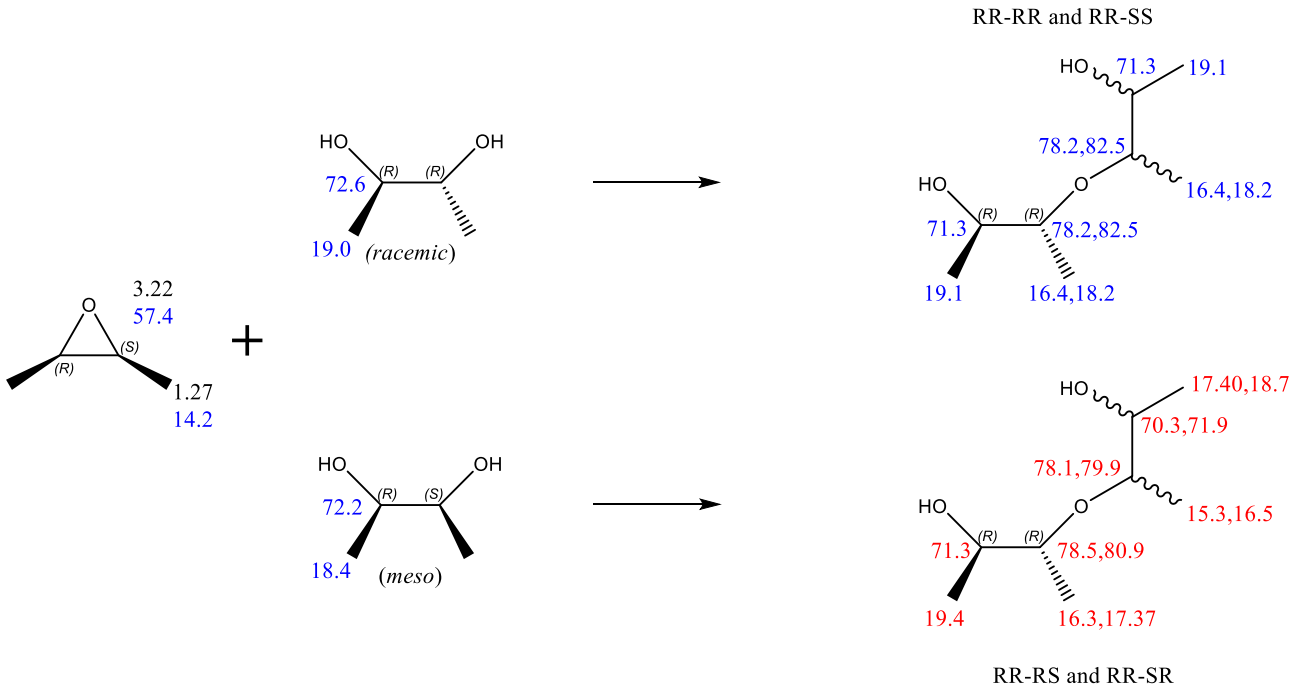

Figure S3. *Cis*-2,3-epoxybutane + 2,3-butanediol reaction NMR assignments in D_2O, referenced to secondary calibration of *racemic* 2,3-butanediol methyl group at 18.98 ppm.

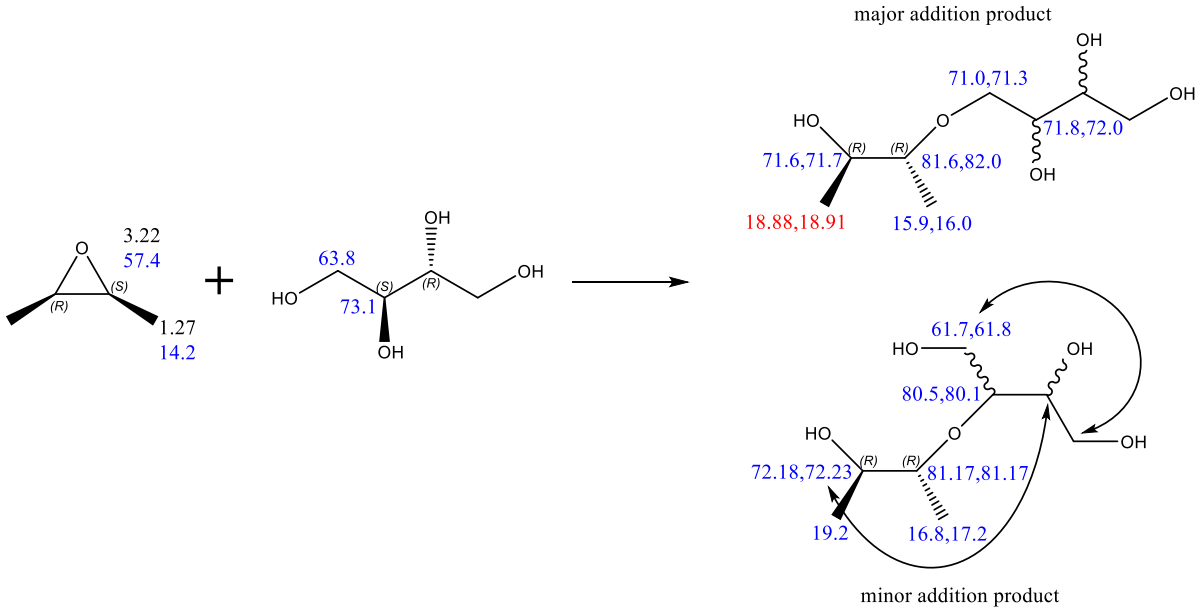

Figure S4. *Cis*-2,3-epoxybutane + *meso*-erythritol reaction NMR assignments in D_2O, referenced to *meso*-erythritol at 63.8 ppm.

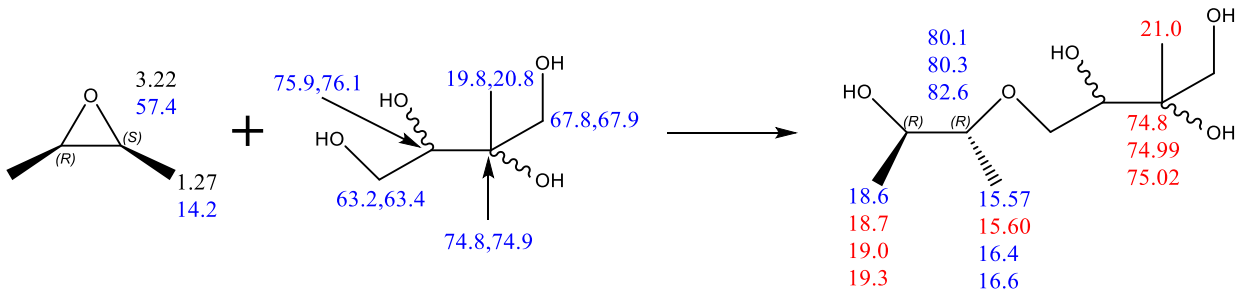

Figure S5. *Cis*-2,3-epoxybutane + 2-methyltetrol reaction NMR assignments in D_2O (assuming the less sterically hindered of the two possible 1° nucleophile linkages), referenced to CHD_2OD at 49.00 ppm.

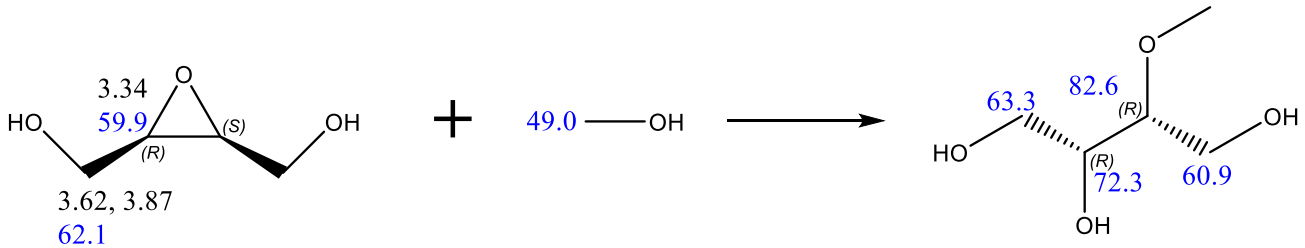

Figure S6. *Cis*-2,3-epoxy-1,4-butanediol + methanol reaction NMR assignments in D_2O, referenced to CHD_2OD at 49.00 ppm.

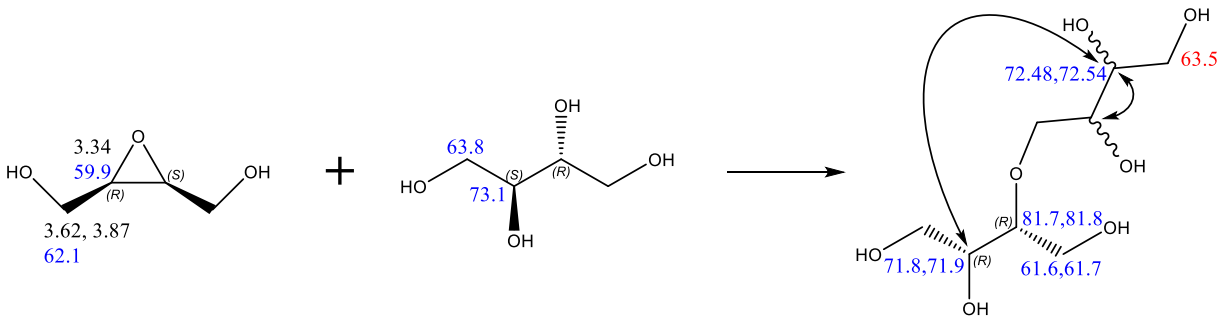

Figure S7. *Cis*-2,3-epoxy-1,4-butanediol + *meso*-erythritol reaction NMR assignments in D_2O, referenced to *meso*-erythritol at 63.8 ppm.

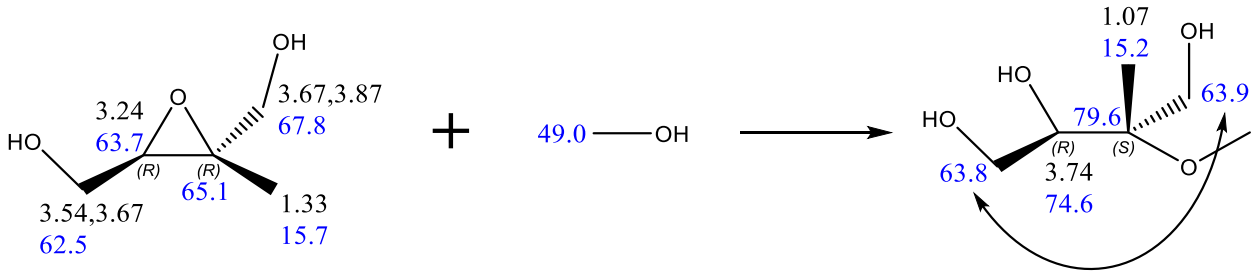

Figure S8. *Trans*-β-IEPOX + methanol reaction ^{1}H NMR and ^{13}C NMR assignments in D_2O. ^{1}H NMR and ^{13}C NMR referenced to CHD_2OD at 3.31 ppm and 49.00 ppm.

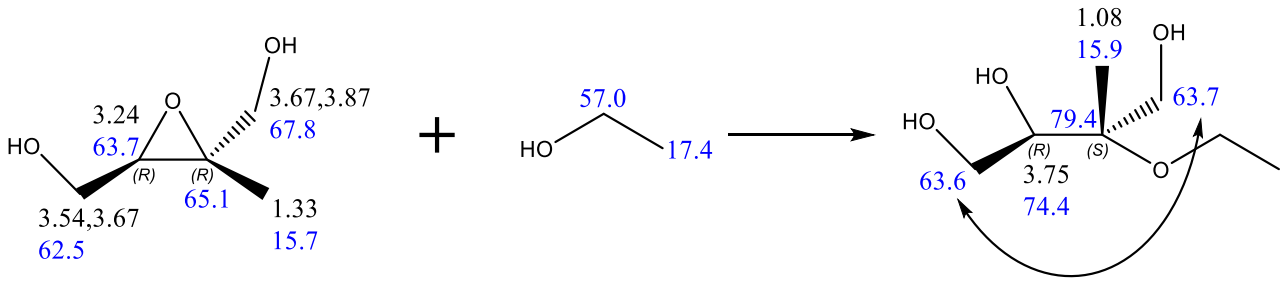

Figure S9. *Trans*-β-IEPOX + ethanol reaction ^{1}H NMR and ^{13}C NMR in ethanol-d_6. ^{1}H NMR and ^{13}C NMR referenced to C_2HD_5O at 3.56 ppm and 56.96 ppm.

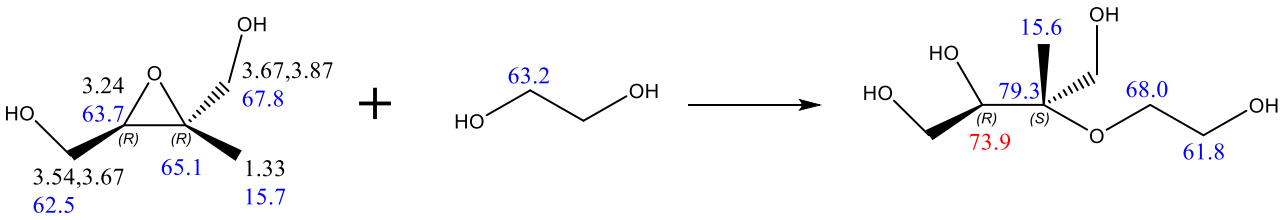

Figure S10. *Trans*-β-IEPOX + ethylene glycol reaction NMR assignments in D_2O, referenced to ethylene glycol at 63.17 ppm.

^{13}C NMR Chemical Shift Differences

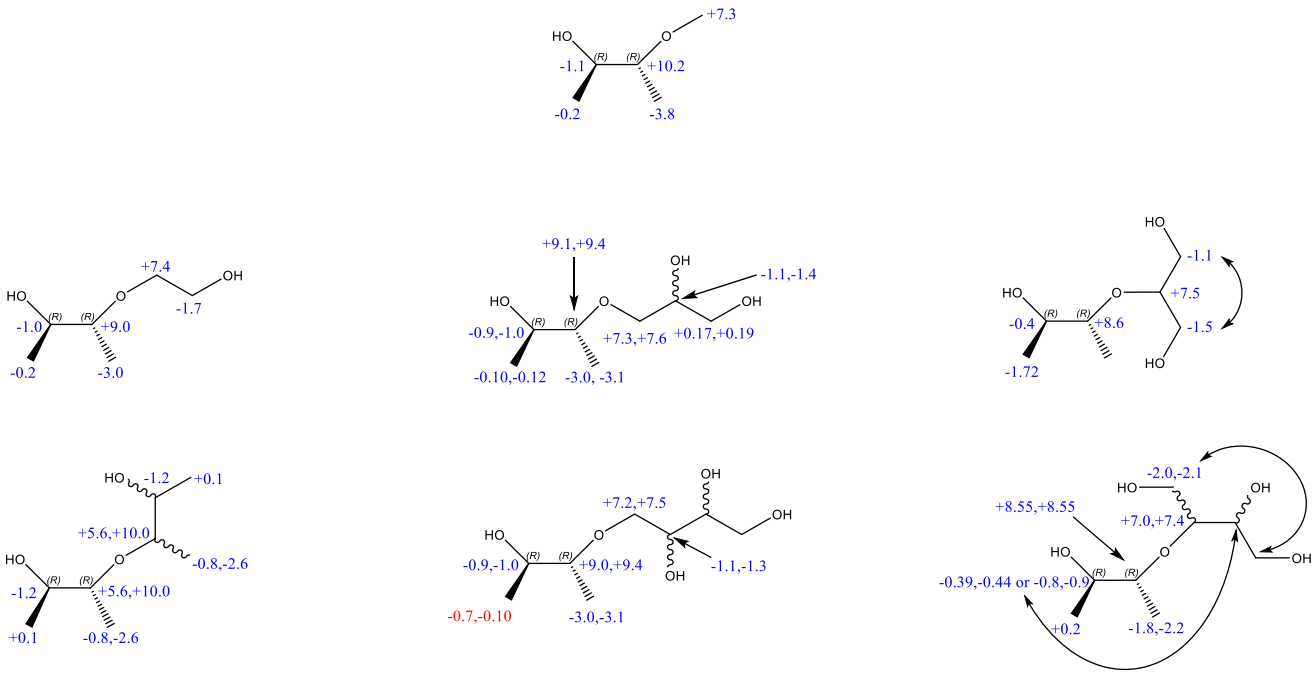

Figure S11. Differences in ^{13}C NMR chemical shift between nucleophiles and the *cis*-2,3-epoxybutane hydrolysis product (*racemic* 2,3-butanediol) and corresponding nucleophilic addition products for *cis*-2,3-epoxybutane systems.

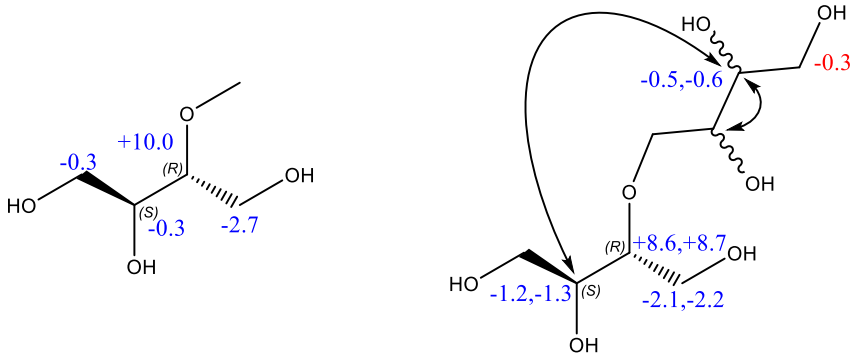

Figure S12. Differences in ^{13}C NMR chemical shift between nucleophiles and the *cis*-2,3-epoxy-1,4-butanediol hydrolysis product (*meso*-erythritol) and corresponding nucleophilic addition products for *cis*-2,3-epoxy-1,4-butanediol systems.

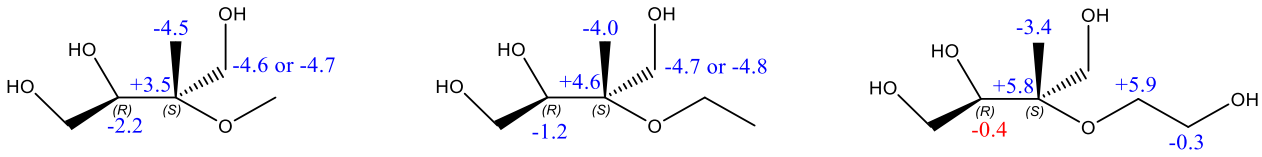

Figure S13. Differences in ^{13}C NMR chemical shift between nucleophiles and the *trans*-β-IEPOX hydrolysis product (2-methylerythritol) and corresponding nucleophilic addition products for *trans*-β-IEPOX systems.

References

1. Minerath, E. C.; Elrod, M. J., Assessing the potential for diol and hydroxy sulfate ester formation from the reaction of epoxides in tropospheric aerosols. *Environ. Sci. Technol.* **2009,** *43*, (5), 1386-1392.
2. Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J., Kinetics of the hydrolysis of atmospherically relevant isoprene-derived hydroxy epoxides. *Environ. Sci. Technol.* **2010,** *44*, 6718-6723.