Delineation of the factors governing reactivity and selectivity in epoxide formation from ammonium ylides and aldehydes

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Supporting information

I. Experimental procedures and analysis data

General information

All air and water sensitive reactions were carried out in oven dried glassware under an argon atmosphere. Solvents were dried by standard methods.[1] NMR spectra were recorded on Jeol 270 MHz or Jeol 400 MHz spectrometers using tetramethylsilane as the internal standard (0.00 ppm). $CDCl_3$ was used as the internal standard for ^{13}C NMR spectra. Flash chromatography was performed using silica gel (Merck Kieselgel 60).

1. General procedure for synthesis of ammonium salts

The appropriate haloalkane (1eq, 10 mmol) was added dropwise over 1 minute to a stirred solution of amine (1 eq, 10 mmol) in THF (50 mL). The reaction mixture was stirred at room temperature for 12 h. The resultant precipitate was collected by suction filtration through sintered glass, washed with THF and Et_2O, and dried under high vacuum. The resulting ammonium salt is then carefully kept under vacuum over P_2O_5.

1-Benzyl-1-azonia-bicyclo[2.2.2]octane chloride:[2] 85%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 1.95 (6H, m, C*H*$_2$), 2.14 (1H, sept, C*H*), 3.49 (6H, m, C*H*$_2$), 4.41 (2H, s, C*H*$_2$), 7.39-7.48 (5H, m, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 133.43, 130.26, 128.98, 127.55, 66.95, 54.10, 24.12, 20.24.

1-(4-Methylbenzyl)-1-azonia-bicyclo[2.2.2]octane:[3] 70%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 1.97 (6H, m, C*H*$_2$), 2.15 (1H, m, C*H*), 2.35 (3H, s, ArC*H*$_3$), 3.77 (6H, m, C*H*$_2$), 4.88 (2H, s, C*H*$_2$), 7.18 (2H, m, Ar*H*), 7.53 (2H, m, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 140.44, 133.23, 129.65, 124.97, 66.87, 53.95, 24.04, 21.24, 20.18.

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1-(4-Chlorobenzyl)-1-azonia-bicyclo[2.2.2]octane chloride:[4] 82%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 1.93 (6H, m, CH_2), 2.15 (1H, sept, C*H*), 3.79 (6H, m, CH_2), 5.02 (2H, s, CH_2), 7.31 (2H, d, *J* = 8.3 Hz, Ar*H*), 7.68 (2H, d, *J* = 8.3 Hz, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 136.65, 134.86, 129.24, 126.07, 65.79, 54.07, 24.04, 20.14.

1-(4-Methoxybenzyl)-1-azonia-bicyclo[2.2.2]octane chloride:[4] 70%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 1.69 (6H, m, CH_2), 1.88 (1H, m, C*H*), 3.47-3.51 (9H, m, CH_2, ArOCH_3), 4.60 (2H, s, CH_2), 6.60 (2H, d, *J* = 8.5 Hz, Ar*H*), 7.33 (2H, d, *J* = 8.5 Hz, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 160.84, 134.62, 119.17, 114.19, 66.45, 55.27, 53.67, 23.93, 20.12.

1-(4-(Trifluoromethyl)benzyl)-1-azonia-bicyclo[2.2.2]octane chloride:[3] 60%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 1.97 (6H, m, CH_2), 2.18 (1H, m, C*H*), 3.83 (6H, m, CH_2), 5.27 (2H, s, CH_2), 7.61 (2H, d, *J* = 8.0 Hz, Ar*H*), 7.90 (2H, d, *J* = 8.0 Hz, Ar*H*). **^{13}C-NMR** δ_C (75.45 MHz; $CDCl_3$): δ 134.14, 132.25 (q, $^2J_{CF}$ = 32 Hz), 131.72, 129.04, 123.62 (q, $^1J_{CF}$ = 272 Hz), 65.70, 54.28, 24.08, 20.13.

1-Benzyl-4-aza-1-azonia-bicyclo[2.2.2]octane chloride:[5] 80%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 3.14 (6H, m, CH_2), 3.45 (6H, m, CH_2), 4.58 (2H, s, CH_2), 7.43-7.46 (5H, m, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 133.48, 130.52, 129.16, 126.81, 67.08, 51.91, 45.54.

1-(4-Methylbenzyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride:[6] 92%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 2.35 (3H, s, ArCH_3), 3.18 (6H, m, CH_2), 3.75 (6H, m, CH_2), 4.99 (2H, s, CH_2), 7.19 (2H, d, *J* = 7.9 Hz, Ar*H*), 7.53 (2H, d, *J* = 7.9 Hz, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 140.69, 133.28, 129.78, 123.59, 67.01, 51.76, 45.44, 21.21.

1-(4-Chlorobenzyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride: [7] 82%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 3.02 (6H, m, CH_2), 3.58 (6H, m, CH_2), 4.95 (2H, s, CH_2), 7.21 (2H, d, *J* = 8.3

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Hz, Ar*H*), 7.53 (2H, d, J = 8.3 Hz, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 136.87, 134.88, 129.39, 125.30, 65.93, 51.84, 45.40.

1-(4-Methoxybenzyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride:[5] 60%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 2.96 (6H, m, CH_2), 3.51-3.58 (9H, m, CH_2, ArOCH_3), 4.77 (2H, s, CH_2), 6.67 (2H, d, J = 8.7 Hz, Ar*H*), 7.38 (2H, d, J = 8.7 Hz, Ar*H*). **^{13}C NMR** δ_C (101 MHz; $CDCl_3$): δ 161.07, 134.75, 118.41, 114.43, 66.76, 55.34, 51.57, 45.40.

1-(4-(trifluoromethyl)-benzyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride: 92%, white solid; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$): δ 3.18 (6H, m, CH_2), 3.78 (6H, m, CH_2), 5.33 (2H, s, CH_2), 7.64 (2H, d, J = 7.9 Hz, Ar*H*), 7.90 (2H, d, J = 7.9 Hz, Ar*H*). **^{13}C-NMR** δ_C (101 MHz; dMeOD): δ 135.21, 133.53 (q, $^2J_{CF}$ = 33 Hz), 132.14, 126.93, 127.00 (q, $^1J_{CF}$ = 272 Hz), 68.17, 53.57, 46.09.

2. General procedure for epoxidation reactions

To an ice cooled stirred solution of the appropriate quaternary ammonium salt (1.eq, 0.42 mmol) and aldehyde (1 eq, 0.42 mmol) in dry THF (5 mL) 0.85 mL of a 1M solution of *t*-BuOK in THF was slowly added (2 eq, 0.48 mmol). After 5 minutes the ice bath was removed and the yellow colored suspension was stirred overnight at r.t. The mixture was diluted with Et_2O (10 mL) and saturated aquous solution of NH_4Cl (2 mL). The two phases were separated and the organic layer was washed with H_2O and then dried over $MgSO_4$. Removal of the solvent under reduced pressure and purification by flash chromatography (2% EtOAc in Petroleum ether) afforded the desired oxide as a colorless solid.

Stilbene oxide:[8] White solid; R_f = 0.70 (10% EtOAc / petroleum ether; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$) *trans isomer*: δ 3.85 (2H, s, C*H*), 7.16-7.37 (10H, m, Ar*H*); *cis isomer*: δ 4.37 (2H, s, C*H*), 7.01-7.15 (10H, m, Ar*H*).

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2-(4-Chlorobenzenyl)3-phenyl oxirane:[8] White solid; R_f = 0.65 (10% EtOAc / petroleum ether; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$) *trans isomer*: δ 3.82 (1H, d, *J* = 1.8 Hz, C*H*), 3.85 (1H, d, *J* = 1.8 Hz, C*H*), 7.04-7.50 (9H, m, Ar*H*); *cis isomer*: δ 4.31 (1H, d, *J* = 4.6 Hz, C*H*), 4.37 (1H, d, *J* = 4.6 Hz, C*H*), 7.04-7.50 (9H, m, Ar*H*).

2-(4-Methylbenzenyl)3-phenyl oxirane:[8] White solid; R_f = 0.70 (10% EtOAc / petroleum ether; **^{1}H NMR** δ_H (400 MHz; $CDCl_3$) *trans isomer*: δ 2.37 (3H, s, CH_3), 3.83 (1H, d, *J* = 1.5 Hz, C*H*), 3.86 (1H, d, *J* = 1.5 Hz, C*H*), 7.16-7.44 (9H, m, Ar*H*); *cis isomer*: δ 2.15 (3H, s, CH_3), 4.24 (2H, m, C*H*), 7.04-7.50 (9H, m, Ar*H*).

2-(4-Methoxylbenzenyl)3-phenyl oxirane:[8] White solid; R_f = 0.50 (10% EtOAc / petroleum ether; **^{1}H-NMR** δ_H (400 MHz; $CDCl_3$) *trans isomer*: δ 3.71 (3H, s, OCH_3), 3.73 (1H, d, *J* = 1.8 Hz, C*H*), 3.78 (1H, d, *J* = 1.8 Hz, C*H*), 6.93-7.41 (9H, m, Ar*H*); *cis isomer*: δ 3.61 (3H, s, OCH_3), 4.23 (1H, d, *J* = 1.6 Hz, C*H*), 4.24 (1H, d, *J* = 1.6 Hz, C*H*), 6.81-7.40 (9H, m, Ar*H*).

2-(4-(Trifluoromethyl)xylbenzenyl)3-phenyl oxirane:[9] White solid; R_f = 0.60 (10% EtOAc / petroleum ether); **^{1}H-NMR** δ_H (400 MHz; $CDCl_3$) *trans isomer*: δ 3.84 (1H, d, *J* = 1.8 Hz, C*H*), 3.92 (1H, d, *J* = 1.7 Hz, C*H*), 7.33-7.41 (5H, m, Ar*H*), 7.46 (2H, d, *J* = 8.1 Hz, Ar*H*),), 7.63 (2H, d, *J* = 8.1 Hz, Ar*H*).

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[9] (a) A. Solladie-Cavallo, P. Lupattelli, C. Bonini, *J. Org. Chem.* **2005**, 70(5), 1605-1611; b) M. Davoust, J-F.Briere, P-A. Jaffres, P. Metzner, *J Org. Chem.* **2005**, 70(10), 4166-4169; c) J. Zanardi, C. Leriverend, D. Aubert, K. Julienne, P. Metzner, *J Org. Chem.* **2001** (2001), 66(16), 5620-5623.

II. Computational details

Computations have been carried out using the Jaguar 4.0 pseudospectral program package. All species have been fully geometry optimized, and the Cartesian coordinates are supplied below. In the case of transition states, the "loose" geometry convergence parameters within Jaguar (which correspond to rms gradients below 0.0015 hartree/au) have been used. Test calculations using the standard convergence criteria led to insignificant changes in structure, but were much more time consuming.

Geometry optimization was carried out using the well established B3LYP hybrid density functional as implemented in Jaguar (optimization of the model reaction (see below) using a more demanding *ab initio* method, MP2, did not lead to significant structure change). The standard split valence polarized 6-31G* basis set was used.

Because of the importance of solvent effects, the optimization was carried out using the polarizable continuum-Poisson method as incorporated in Jaguar. Parameters used for the continuum solvent are: a dielectric constant of 7.43, and a solvent probe radius of 2.52251 Å, which are suitable for THF, the solvent used in these reactions.

Results on the model reaction between formaldehyde and Me_3NCH_2 (see below) reveal significant discrepancies in computed energies according to the method used. A large influence of basis set size is also observed. Taking the accurate G3(MP2)/B3LYP energies as a reference, we find however that B3LYP/6-311+G** energies describe well the reaction under study. Accordingly, all given energies are obtained after corresponding single point calculations at the B3LYP/6-311+G**(THF) level using the fine grid and high accuracy parameters within Jaguar. Even at this level, however, the gas-phase stability of betaine intermediates is exaggerated by about 2 kcal/mol, and energy of elimination TS underestimated by about 3 kcal/mol, as compared to that of reactants.

Frequency calculations for large molecules of the type studied here, especially if solvation effects need to be taken into account, are of prohibitive computational expense and have not been performed, so that we cannot be absolutely certain that the optimized structures have the desired character as minima or transition states, and cannot either include zero-point energy or thermal corrections. However, given the low symmetry of the molecules, it is extremely unlikely that the optimized structures correspond to anything else than minima or transition states. Zero-point energy corrections are expected to be fairly small and to be near identical for isomeric pathways leading to *cis* and *trans* aziridine so that their neglect should be of little consequence.

There are usually several local minima or saddle points corresponding to each intermediate or transition state. This is due to the possibility of multiple conformations of substituents. We have

systematically optimized several different local minima and saddle points. The data presented refer to the lowest energy form found, unless mentioned otherwise.

III. Model reaction results

Relative energies (kcal/mol) of the stationary points (geometries optimized at the B3LYP/6-31G*(THF) level of theory) for the model reaction $CH_2NMe_3 + CH_2=O$.

method	*cisoid* betaine	*transoid* betaine	elimination TS	products
B3LYP/6-31G*	-46.3	-29.1	-33.8	-64.0
B3LYP/6-311+G**	-38.0	-24.5	-26.4	-54.2
MP2/6-31G*	-50.0	-31.0	-35.3	-63.8
MP2/6-311+G**	-42.4	-27.7	-25.5	-51.0
QCISD(T)/6-31G*	-48.4	-30.0	-35.5	-63.0
G3(MP2)	-36.1	-22.6	-23.3	-47.7
B3LYP/6-31G*(THF)	-53.9	-48.1	-36.9	-58.0
B3LYP/6-311+G**(THF)	-47.4	-46.9	-28.1	-45.6

IV. Energies and geometries

All geometries have been optimized at the B3LYP/6-31G* level of theory including a continuum description of THF solvent. Energies are given in a.u., geometries as Cartesian coordinates in Å.

A. Model reaction : $CH_2O + Me_3NCH_2$

Me_3NCH_2

E(B3LYP 6-31G*) = -213.658399
E(B3LYP 6-311+G**) = -213.735901
E(B3LYP 6-31G*(THF)) = -213.672131
E(B3LYP 6-311+G**(THF)) = -213.753082

H	2.22210	.05091	0.00000
C	1.35402	.69227	0.00000
H	1.35059	1.76853	0.00000
N	.05416	.01869	0.00000
C	-.14512	-.86058	1.22045
H	-.06804	-.21966	2.09806
H	-1.11211	-1.37911	1.19137
H	.66651	-1.59031	1.23582
C	-.14512	-.86058	-1.22045
H	.66651	-1.59031	-1.23582
H	-1.11211	-1.37911	-1.19137
H	-.06804	-.21966	-2.09806
C	-1.02222	1.05954	0.00000
H	-2.00514	.58302	0.00000
H	-.89375	1.67554	.89163
H	-.89375	1.67554	-.89163

CH_2O

E(B3LYP 6-31G*) = -114.500530
E(B3LYP 6-311+G**) = -114.541590
E(B3LYP 6-31G*(THF)) = -114.506546
E(B3LYP 6-311+G**(THF)) = -114.549549

C	-1.070721	1.46303	-.222153
H	-.379115	1.19114	-1.042097
O	-1.063662	2.56567	.282754
H	-1.767929	.66928	.108282

***Cisoid* betaine**

E(B3LYP 6-31G*) = -328.232721
E(B3LYP 6-311+G**) = -328.338074
E(B3LYP 6-31G*(THF)) = -328.264605
E(B3LYP 6-311+G**(THF)) = -328.378186

C	.45993	1.31139	-.46475
C	-.75094	2.26016	-.70525
H	1.13191	1.28660	-1.32733
H	-1.17521	1.85252	-1.66674
O	-.46763	3.57379	-.70091
H	.12702	.29201	-.24162
H	-1.51683	1.94394	.05613
N	1.34137	1.75709	.70880
C	2.22377	2.89070	.23989
H	2.92688	2.49517	-.49652
H	1.53956	3.61539	-.21131
H	2.76462	3.29187	1.10038
C	.49411	2.25142	1.85315
H	-.04520	3.12338	1.47917
H	-.19331	1.45827	2.15262
H	1.15492	2.50970	2.68326
C	2.18861	.60777	1.16322
H	2.88071	.95998	1.93174
H	1.54013	-.17106	1.56983
H	2.74418	.22134	.30630

***Transoid* betaine**

E(B3LYP 6-31G*) = -328.205282
E(B3LYP 6-311+G**) = -328.316528
E(B3LYP 6-31G*(THF)) = -328.255362
E(B3LYP 6-311+G**(THF)) = -328.377345

C	.35282	.78996	.19794
C	-1.04597	1.32317	-.22584
H	.50291	1.01470	1.25698
H	-1.20010	1.02618	-1.30317
O	-1.06894	2.63684	.02258
H	1.11580	1.31382	-.38352
H	-1.81590	.70621	.32283
N	.66502	-.71207	.04016
C	-.26784	-1.52795	.89387
H	-.16420	-1.20467	1.93160
H	-1.29156	-1.36679	.55728
H	-.00088	-2.58253	.79905
C	.52244	-1.12172	-1.40019
H	-.51471	-.99171	-1.70674
H	1.16973	-.48672	-2.00791
H	.81846	-2.16795	-1.50082
C	2.08011	-.95975	.48326
H	2.30193	-2.02599	.39614
H	2.75209	-.38069	-.15292
H	2.18049	-.63631	1.52080

Elimination TS

E(B3LYP 6-31G*) = -328.212794
E(B3LYP 6-311+G**) = -328.319484
E(B3LYP 6-31G*(THF)) = -328.237416
E(B3LYP 6-311+G**(THF)) = -328.347444

C	.29283	1.03224	.21237
C	-.99701	1.45882	-.35493
H	.36093	.97819	1.29181
H	-1.09033	1.34785	-1.45191
O	-.61667	2.70215	.10915
H	1.18558	1.32635	-.32553
H	-1.89256	1.00774	.11311
N	.69073	-.96391	-.00905
C	-.37097	-1.69726	.69775
H	-.38614	-1.39126	1.74815
H	-1.33850	-1.45826	.24856
H	-.21058	-2.78412	.64593
C	.68899	-1.24666	-1.45279
H	-.29435	-1.00914	-1.86657
H	1.43796	-.61945	-1.94547
H	.91780	-2.30276	-1.65798
C	2.01055	-1.20895	.59113
H	2.29973	-2.26761	.51350
H	2.76048	-.59862	.07862
H	1.98532	-.92567	1.64775

Ethylene oxide

E(B3LYP 6-31G*) = -153.786373
E(B3LYP 6-311+G**) = -153.835933
E(B3LYP 6-31G*(THF)) = -153.792386
E(B3LYP 6-311+G**(THF)) = -153.843177

C	.28856	1.01892	.21269
C	-1.00177	1.40876	-.37403
H	.31127	.49817	1.17034
H	-1.09052	1.52367	-1.45442
O	-.16451	2.38228	.27340

H 1.14786 .84480 -.43529
H -1.92796 1.17304 .15015

NMe_3

E(B3LYP 6-31G*) = -174.474628
E(B3LYP 6-311+G**) =
-174.527855
E(B3LYP 6-31G*(THF)) =
-174.478731
E(B3LYP 6-311+G**(THF)) =
-174.532151

N 0.00000 0.00000 .35174
C -.69603 -1.20556 -.08770
H -1.72059 -1.20599 .30284
H -.75138 -1.30143 -1.19047
H -.18412 -2.09308 .30284
C -.69603 1.20556 -.08770
H -1.72059 1.20599 .30284
H -.18412 2.09308 .30284
H -.75138 1.30143 -1.19047
C 1.39206 0.00000 -.08770
H 1.50277 0.00000 -1.19047
H 1.90472 .88708 .30284
H 1.90472 -.88708 .30284

B. $PhCHNMe_3$ + PhCHO

$PhCHNMe_3$

E(B3LYP 6-31G*) = -444.739143
E(B3LYP 6-311+G**) =
-444.863640
E(B3LYP 6-31G*(THF)) =
-444.759529
E(B3LYP 6-311+G**(THF)) =
-444.884695

C 1.15810 1.72453 0.00000
C .30295 .56073 0.00000
C -1.10356 .86553 0.00000
C -1.57630 2.17845 0.00000
C -.71753 3.27968 0.00000
C .66624 3.01695 0.00000
H 2.23639 1.56682 0.00000
H -1.84436 .07148 0.00000
H -2.65500 2.33626 0.00000
H -1.09935 4.29712 0.00000
H 1.37385 3.84616 0.00000
C .92686 -.69749 0.00000
H 2.00319 -.79198 0.00000
N .23952 -2.01781 0.00000
C -.61050 -2.22736 -1.23686
H .05069 -2.18612 -2.10214
H -1.11328 -3.19695 -1.18237
H -1.34381 -1.42630 -1.30119
C -.61050 -2.22736 1.23686
H -1.34381 -1.42630 1.30119
H -1.11328 -3.19695 1.18237
H .05069 -2.18612 2.10214
C 1.29790 -3.08720 0.00000
H .81728 -4.06758 0.00000
H 1.91200 -2.96259 -.89339
H 1.91200 -2.96259 .89339

PhCHO

E(B3LYP 6-31G*) = -345.573169
E(B3LYP 6-311+G**) =
-345.668641
E(B3LYP 6-31G*(THF)) =
-345.582485
E(B3LYP 6-311+G**(THF)) =
-345.678878

C -1.08521 .81781 .00000
C -.37224 -.39014 .00000
C 1.03330 -.37872 .00000
C 1.71426 .83481 .00000
C .99743 2.03976 .00000
C -.40084 2.03293 .00000
H -2.17343 .79621 .00000
H 1.57052 -1.32313 .00000
H 2.80116 .84981 .00000
H 1.53240 2.98620 .00000
H -.95191 2.96937 .00000
C -1.12019 -1.65976 .00000
O -.61000 -2.77108 .00000
H -2.22418 -1.55222 .00000

***Cisoid syn* betaine**

E(B3LYP 6-31G*) = -790.272252
E(B3LYP 6-311+G**) =
-790.551437
E(B3LYP 6-31G*(THF)) =
-790.368103
E(B3LYP 6-311+G**(THF)) =
-790.585354

C .36251 1.28146 .09960
C -.73609 2.22764 -.60240
C 1.60116 1.06472 -.73811
H -.12039 3.04573 -1.05721
C 1.97514 -.24734 -1.07069
C 3.06615 -.49969 -1.90312
C 3.81526 .56270 -2.41511
C 3.45696 1.87433 -2.09477
C 2.35754 2.12468 -1.27054
O -1.69068 2.66727 .22869
H -.10152 .31087 .29322
H 1.39319 -1.08047 -.68176
H 3.32995 -1.52499 -2.15125
H 4.66683 .37066 -3.06324
H 4.02827 2.70932 -2.49342
H 2.08466 3.15519 -1.06463
N .68564 1.78415 1.56137
C .82340 3.28518 1.63058
H 1.65498 3.59677 .99882
H -.12854 3.69503 1.28847
H 1.03151 3.55881 2.66743
C -.47130 1.36891 2.44552
H -1.36769 1.73417 1.93678
H -.46379 .27962 2.52840
H -.33152 1.82082 3.43066
C 1.93539 1.15046 2.10085
H 2.02233 1.42181 3.15569
H 1.85797 .06624 2.00339
H 2.80127 1.51240 1.54788
C -2.45590 .00606 -3.94827
C -1.32205 .79535 -4.15822
C -.74590 1.49472 -3.09294
C -1.29072 1.42071 -1.80491
C -2.43335 .63446 -1.61008
C -3.01035 -.07307 -2.66582
H -2.91109 -.53130 -4.77747
H -.89238 .87649 -5.15475
H .13077 2.11488 -3.26865
H -2.87979 .62519 -.61971
H -3.90197 -.67361 -2.49463

***Cisoid anti* betaine**

E(B3LYP 6-31G*) = -790.340487
E(B3LYP 6-311+G**) =
-790.552932
E(B3LYP 6-31G*(THF)) =
-790.368820
E(B3LYP 6-311+G**(THF)) =
-790.585509

C .33110 1.18472 .14250
C -.94187 2.02325 -.32418
C 1.48898 1.17195 -.83148
C -1.35561 1.52940 -1.73606
C -1.77130 .21365 -1.98314
C -2.19526 -.17783 -3.25545
C -2.21766 .74905 -4.30355
C -1.81702 2.06589 -4.06336
C -1.39350 2.44798 -2.78794
C 2.14726 -.03592 -1.11273
C 3.17324 -.09308 -2.05950
C 3.55501 1.06255 -2.74471
C 2.89563 2.26860 -2.48552
C 1.87113 2.32472 -1.54089
O -.78261 3.35046 -.20946
H .02669 .15071 .33546
H -1.75516 1.60966 .33162
H -1.78248 -.51290 -1.17055
H -2.51835 -1.20253 -3.42887
H -2.55392 .44819 -5.29352
H -1.84279 2.79774 -4.86902
H -1.10002 3.46931 -2.56697
H 1.84261 -.94560 -.59848
H 3.66766 -1.04007 -2.26407

H 4.35321 1.02204 -3.48245
H 3.17407 3.16884 -3.02904
H 1.32284 3.24311 -1.36217
N .78006 1.66839 1.58210
C 1.53011 2.97878 1.53013
H 2.48536 2.82098 1.03205
H .88774 3.65662 .96606
H 1.69365 3.31483 2.55669
C -.42600 1.86994 2.46512
H -.98241 2.71491 2.06237
H -1.02910 .96030 2.46357
H -.07297 2.07973 3.47708
C 1.65847 .62418 2.20842
H 2.00173 .99426 3.17704
H 1.08231 -.29331 2.34400
H 2.51271 .43888 1.55766

Syn torsional TS

E(B3LYP 6-31G*) = -790.303890
E(B3LYP 6-311+G**) =
-790.525030
E(B3LYP 6-31G*(THF)) =
-790.346336
E(B3LYP 6-311+G**(THF)) =
-790.573182

C .44585 .84680 -.05040
C -1.05470 1.43899 -.36348
H .70907 1.46649 .80621
C -1.45683 1.38834 -1.85853
C -2.31077 .41140 -2.38249
C -2.75477 .47095 -3.71017
C -2.34634 1.51901 -4.53639
C -1.50405 2.51218 -4.01963
C -1.07836 2.44941 -2.69481
O -1.08292 2.66910 .12768
H -1.75007 .69625 .12942
H -2.67169 -.39013 -1.73803
H -3.43376 -.29038 -4.08978
H -2.69489 1.57540 -5.56551
H -1.19462 3.34382 -4.65014
H -.46827 3.23834 -2.26610
N .50224 -.60532 .60004
C -.21481 -.55629 1.92785
H .27358 .18396 2.56338
H -1.25643 -.28247 1.76877
H -.15400 -1.54378 2.39009
C -.13518 -1.66349 -.25353
H -1.16727 -1.38013 -.45179
H .42086 -1.75568 -1.18492
H -.10573 -2.61239 .28677
C 1.92940 -.99977 .87678
H 1.93018 -1.94204 1.42991
H 2.45956 -1.11591 -.06697
H 2.40010 -.21660 1.47363
C 3.48102 1.61585 -3.04697
C 2.46691 .69483 -3.32366
C 1.48127 .42185 -2.37411
C 1.50263 1.04460 -1.11270
C 2.53014 1.96679 -.85141
C 3.50479 2.25890 -1.80794
H 4.23932 1.83678 -3.79441
H 2.42900 .20053 -4.29133
H .67418 -.25216 -2.64046
H 2.55727 2.47224 .11112
H 4.28142 2.98620 -1.58268

***Anti* torsional TS**

E(B3LYP 6-31G*) = -790.302994
E(B3LYP 6-311+G**) =
-790.527058
E(B3LYP 6-31G*(THF)) =
-790.348643
E(B3LYP 6-311+G**(THF)) =
-790.572996

C .39773 .98929 .25311
C -1.07338 1.53965 -.15418
C 1.06207 1.82817 1.32378
C -1.32927 1.35319 -1.67095
C -2.50267 .74897 -2.13963
C -2.82535 .74423 -3.50172
C -1.96669 1.34153 -4.42653
C -.78912 1.95046 -3.97335
C -.48312 1.96151 -2.61284
C 2.40168 2.21265 1.17035
C 3.04399 3.00552 2.12776
C 2.34637 3.42732 3.25987
C 1.00551 3.05986 3.42178
C .36532 2.27975 2.45876
O -1.20114 2.82216 .16271
H 1.03637 1.00517 -.63433
H -1.80601 .84240 .35245
H -3.18814 .29598 -1.42318
H -3.75126 .28079 -3.83746
H -2.21402 1.34486 -5.48574
H -.11712 2.42921 -4.68333
H .40840 2.48231 -2.26901
H 2.94934 1.90303 .28196
H 4.08194 3.29554 1.98209
H 2.83744 4.04700 4.00677
H .45015 3.40101 4.29238
H -.68566 2.04425 2.57263
N .43101 -.55279 .62925
C -.28830 -.84160 1.92091
H .22003 -.32360 2.73278
H -1.31862 -.49655 1.84109
H -.26629 -1.91980 2.09261
C -.21004 -1.35485 -.47208
H -1.26990 -1.11514 -.52133
H .27182 -1.10275 -1.41736
H -.07434 -2.41554 -.25041
C 1.85519 -1.02276 .76727
H 1.84924 -2.08848 1.00719
H 2.37261 -.85788 -.17954
H 2.34187 -.46108 1.56265

***Transoid syn* betaine**

E(B3LYP 6-31G*) = -790.225068
E(B3LYP 6-311+G**) =
-790.525864
E(B3LYP 6-31G*(THF)) =
-790.349662
E(B3LYP 6-311+G**(THF)) =
-790.572978

C .44414 .82543 -.04726
C -1.00427 1.47094 -.37559
H .51838 1.06098 1.01525
C -1.44462 1.46203 -1.85963
C -2.27432 .46916 -2.39790
C -2.76057 .56018 -3.70786
C -2.42543 1.65956 -4.50146
C -1.61333 2.66876 -3.96942
C -1.14254 2.57303 -2.66028
O -.92896 2.69454 .13835
H -1.73097 .77882 .13197
H -2.58512 -.36887 -1.77312
H -3.41776 -.21452 -4.09801
H -2.80996 1.74210 -5.51579
H -1.36571 3.54064 -4.57224
H -.56019 3.36985 -2.20941
N .61444 -.77063 .00973
C -.48297 -1.34714 .86602
H -.52822 -.79106 1.80380
H -1.43487 -1.26995 .34465
H -.25141 -2.39597 1.06527
C .57661 -1.43453 -1.33588
H -.31942 -1.11284 -1.86487
H 1.46584 -1.15288 -1.89756
H .56003 -2.51699 -1.18904
C 1.92500 -1.10164 .67319
H 2.02025 -2.18794 .74317
H 2.73921 -.68859 .07981
H 1.93216 -.66281 1.67274
C 3.77882 2.84990 -1.94839
C 2.89456 2.10376 -2.73025
C 1.81968 1.43357 -2.14039
C 1.61173 1.48674 -.75120
C 2.50921 2.24585 .01900
C 3.57993 2.92201 -.56751
H 4.61021 3.37633 -2.41120
H 3.03077 2.05115 -3.80770
H 1.12777 .89665 -2.77836
H 2.35674 2.31652 1.09306
H 4.25331 3.50862 .05304

***Transoid anti* betaine**

E(B3LYP 6-31G*) = -790.258708
E(B3LYP 6-311+G**) =
-790.529239
E(B3LYP 6-31G*(THF)) =
-790.350115
E(B3LYP 6-311+G**(THF)) =
-790.575132

C	0.39994	0.92148	0.22416
C	-0.97780	1.60438	-0.19318
C	0.68948	1.23497	1.68327
C	-1.37253	1.45041	-1.67626
C	-2.48977	0.70875	-2.07923
C	-2.90418	0.69159	-3.41724
C	-2.19700	1.41738	-4.37623
C	-1.08251	2.17155	-3.98459
C	-0.68823	2.19577	-2.64897
C	1.94018	1.75438	2.04787
C	2.24322	2.05082	3.37839
C	1.29458	1.82715	4.37779
C	0.04131	1.31501	4.03007
C	-0.25783	1.02435	2.69881
O	-0.80793	2.88540	0.13987
H	1.17620	1.37592	-0.39630
H	-1.77563	1.05141	0.37758
H	-3.06581	0.16302	-1.33209
H	-3.78708	0.12385	-3.70403
H	-2.51837	1.41393	-5.41526
H	-0.53624	2.75576	-4.72259
H	0.13572	2.82633	-2.32723
H	2.68177	1.94803	1.27557
H	3.21749	2.46297	3.63062
H	1.52360	2.06020	5.41479
H	-0.71379	1.15458	4.79600
H	-1.25320	0.66752	2.45066
N	0.63611	-0.65419	-0.06383
C	-0.52428	-1.47895	0.41181
H	-0.65697	-1.32116	1.48154
H	-1.42104	-1.17739	-0.12676
H	-0.30829	-2.53242	0.21871
C	0.82003	-0.87174	-1.54131
H	-0.07631	-0.55345	-2.06601
H	1.67606	-0.28470	-1.87823
H	1.00520	-1.93384	-1.71681
C	1.88472	-1.14720	0.61676
H	2.06357	-2.18038	0.30874
H	2.72361	-0.51938	0.31263
H	1.75498	-1.09406	1.69564

Syn elimination TS

E(B3LYP 6-31G*) = -790.314569
E(B3LYP 6-311+G**) =
-790.529722
E(B3LYP 6-31G*(THF)) =
-790.345371
E(B3LYP 6-311+G**(THF)) =
-790.562514

C	.36410	.95607	-.02524
C	-1.04749	1.42705	-.40604
H	.43657	.98496	1.05740
C	-1.50525	1.43517	-1.87257
C	-2.25627	.38987	-2.42638
C	-2.73122	.46092	-3.74024
C	-2.47282	1.59400	-4.51681
C	-1.75182	2.65742	-3.96329
C	-1.28255	2.57881	-2.65123
O	-.84494	2.66026	.12073
H	-1.78579	.79203	.13747
H	-2.50264	-.47872	-1.81634
H	-3.31781	-.35850	-4.15005
H	-2.84716	1.65702	-5.53622
H	-1.56848	3.55475	-4.55127
H	-.75215	3.40644	-2.19214
N	.67675	-.98779	-.01751
C	-.41758	-1.56025	.80045
H	-.45160	-1.04999	1.76679
H	-1.37156	-1.42388	.29010
H	-.24613	-2.63132	.96685
C	.68239	-1.56728	-1.37778
H	-.26155	-1.33665	-1.87387
H	1.50425	-1.13348	-1.94992
H	.81390	-2.65591	-1.32783
C	1.97588	-1.22350	.65281
H	2.13969	-2.29887	.79907
H	2.78156	-.81234	.04276
H	1.97368	-.72766	1.62743
C	3.87715	2.64323	-1.88688
C	2.88145	2.07138	-2.68227
C	1.73979	1.51861	-2.09820
C	1.56545	1.53223	-.70185
C	2.58621	2.09671	.08506
C	3.72655	2.65116	-.49697
H	4.76181	3.07915	-2.34531
H	2.98880	2.05806	-3.76434
H	.97702	1.09060	-2.73687
H	2.46983	2.12200	1.16585
H	4.49336	3.09590	.13305

Anti elimination TS

E(B3LYP 6-31G*) = -790.318907
E(B3LYP 6-311+G**) =
-790.532905
E(B3LYP 6-31G*(THF)) =
-790.347429
E(B3LYP 6-311+G**(THF)) =
-790.565608

C	.36860	1.07514	.22332
C	-.98791	1.61300	-.22428
C	.69274	1.25747	1.67064
C	-1.39401	1.42190	-1.68917
C	-2.51054	.65918	-2.05293
C	-2.92447	.58020	-3.38800
C	-2.22330	1.27096	-4.37833
C	-1.11285	2.04742	-4.02384
C	-.71219	2.12873	-2.69074
C	1.98553	1.65647	2.04936
C	2.32122	1.83491	3.39256
C	1.36820	1.60882	4.38872
C	.07881	1.20457	4.02742
C	-.25533	1.02866	2.68486
O	-.64696	2.89290	.07935
H	1.16312	1.39519	-.44650
H	-1.80292	1.16960	.39204
H	-3.08391	.14713	-1.28066
H	-3.80395	-.00444	-3.64940
H	-2.54809	1.22223	-5.41522
H	-.57389	2.60514	-4.78715
H	.11167	2.77390	-2.39933
H	2.72812	1.85432	1.27918
H	3.32417	2.15996	3.65935
H	1.62299	1.75471	5.43570
H	-.67401	1.03633	4.79405
H	-1.27120	.74341	2.42679
N	.69496	-.83449	-.08793
C	-.51914	-1.57917	.31601
H	-.72206	-1.38817	1.37205
H	-1.36518	-1.24366	-.28517
H	-.37405	-2.65711	.16763
C	.95715	-.99667	-1.53772
H	.10231	-.63090	-2.10526
H	1.84471	-.41903	-1.80930
H	1.13104	-2.05415	-1.77393
C	1.86766	-1.31012	.68180
H	2.07746	-2.35836	.43132
H	2.73948	-.70068	.43145
H	1.66650	-1.22684	1.75029

Cis epoxide

E(B3LYP 6-31G*) = -615.901300
E(B3LYP 6-311+G**) =
-616.059644
E(B3LYP 6-31G*(THF)) =
-615.912051
E(B3LYP 6-311+G**(THF)) =
-616.069988

C	-.52954	.18758	-.41588
C	.87797	-.28916	-.27054
O	.45053	.95886	.29993
H	-1.25237	-.30608	.23796
H	1.02292	-1.07665	.47308
C	-2.33727	1.75922	-3.98584
C	-2.71325	.50928	-3.48152
C	-2.11311	.01454	-2.32381
C	-1.12335	.75635	-1.66106
C	-.75856	2.01093	-2.16487
C	-1.36166	2.50753	-3.32318
H	-2.80890	2.14950	-4.88446
H	-3.47822	-.07622	-3.98589
H	-2.41626	-.95241	-1.92546
H	-.01874	2.60487	-1.63872
H	-1.07262	3.48500	-3.70324
C	3.87927	-.34249	-3.34823
C	3.48615	.87708	-2.79206
C	2.50711	.91441	-1.79556
C	1.90938	-.27014	-1.34893
C	2.31836	-1.49355	-1.90111
C	3.29364	-1.53051	-2.89712
H	4.64354	-.37028	-4.12106
H	3.94664	1.80344	-3.12795
H	2.22160	1.86036	-1.34680
H	1.87293	-2.42005	-1.54256
H	3.60141	-2.48555	-3.31657

***Trans* epoxide**

E(B3LYP 6-31G*) = -615.906194
E(B3LYP 6-311+G**) =
-616.064210
E(B3LYP 6-31G*(THF)) =
-615.917519
E(B3LYP 6-311+G**(THF)) =
-616.074542

C	-.64062	-.07915	-.37667
C	.83543	.01395	-.18608
O	-.02217	1.14284	.06068
C	-1.53809	-.77145	.59326
C	-1.50328	-.46150	1.96029
C	-2.34357	-1.12709	2.85456
C	-3.22584	-2.10981	2.39329
C	-3.26653	-2.42018	1.03074
C	-2.42957	-1.75136	.13452
H	-.99746	-.05041	-1.40755
H	1.23254	-.44553	.72070
H	-.83077	.31584	2.31325
H	-2.31401	-.87393	3.91182
H	-3.88195	-2.62564	3.09051
H	-3.95498	-3.17820	.66436
H	-2.46993	-1.98794	-.92723
C	3.62608	.29988	-3.44289
C	3.81824	-.64087	-2.42706
C	2.91102	-.72367	-1.36824
C	1.79818	.12709	-1.31951
C	1.61226	1.07195	-2.33908
C	2.52185	1.15713	-3.39425
H	4.33546	.36938	-4.26419
H	4.67835	-1.30563	-2.45482
H	3.06774	-1.45036	-.57309
H	.76627	1.75215	-2.28968
H	2.37206	1.89795	-4.17622