Supplementary Material for

A computational study of the influence of methyl substituents on competitive ring closure to α- and β-lactones

Philippe B. Wilson and Ian H. Williams

MP2(fc)/6-31+G(d) : vacuum

1a
Electronic Energy = -913.5619752
Enthalpy 298K = -913.480685
Free Energy 298K, 1 atm = -913.526886

O	2.170082	-0.374944	-1.678633
C	0.888408	-0.303477	0.367269
H	0.698758	-1.015070	1.178253
H	1.198648	0.646168	0.828946
C	2.092637	-0.798716	-0.483350
O	2.929234	-1.536700	0.138609
C	-0.402406	-0.004311	-0.380359
H	-0.168226	0.529573	-1.301179
C	-1.392744	0.834699	0.479441
O	-2.194254	0.235037	1.253771
O	-1.222397	2.090424	0.330837
Cl	-1.162155	-1.571585	-0.940377

3a‡
Electronic Energy = -913.5275072
Enthalpy 298K = -913.448474
Free Energy 298K, 1 atm = -913.494620
Imaginary Frequency = 339.9i cm^{-1}

C	1.140739	1.402185	0.025094
O	2.227982	1.708690	-0.474280
C	0.338163	0.185231	0.234102
C	-0.767530	-0.164742	-0.699722
H	-0.567521	-1.174082	-1.075196
H	-0.781329	0.516975	-1.555564
Cl	1.905674	-1.794476	-0.041701
O	0.183835	2.097888	0.558417
C	-2.195052	-0.219283	-0.053807
O	-3.142204	0.010608	-0.872447
O	-2.261787	-0.542600	1.168041
H	0.263507	-0.197294	1.243026

3a
Electronic Energy = -453.9434414
Enthalpy 298K = -453.865921
Free Energy 298K, 1 atm = -453.907229

C	-0.608812	-0.248227	0.562463
C	0.622700	-0.723060	-0.129174
C	-1.844210	0.083306	-0.111132
C	1.561609	-1.553644	0.809127
H	0.369933	-1.286585	-1.033614
H	1.192049	0.164912	-0.444425
O	-1.916062	-1.159778	0.374145
H	-0.479102	0.008439	1.612372
O	-2.565079	0.827436	-0.748751
O	1.480552	-1.259865	2.040736
O	2.313444	-2.373701	0.212191

4a‡
Electronic Energy = -913.523246
Enthalpy 298K = -913.443840
Free Energy 298K, 1 atm = -913.488288
Imaginary Frequency = 509.5i cm^{-1}

O	1.726152	0.622372	-0.854256
C	0.722817	-0.995122	0.341066
H	0.608815	-2.041180	0.044741
H	0.546599	-0.893074	1.415160
C	2.044860	-0.390069	-0.099145
O	3.188102	-0.812219	0.192671
C	-0.167914	-0.056905	-0.421591
H	-0.339649	-0.212707	-1.475834
C	-0.679102	1.260202	0.193422
O	-1.230100	2.050503	-0.631212
O	-0.457278	1.406973	1.433791
Cl	-2.162560	-1.405415	-0.166177

4a
Electronic Energy = -453.9697842
Enthalpy 298K = -453.891025
Free Energy 298K, 1 atm = -453.931732

C	-0.269052	0.422264	0.587887
C	0.678753	1.095305	-0.415727
C	-1.568012	-0.129936	-0.031709
C	1.641875	-0.007241	-0.019470
H	1.028490	2.103227	-0.174530
H	0.347680	1.038049	-1.455549
O	-1.444749	-1.127131	-0.793602
O	-2.580728	0.578940	0.258919
O	2.784052	-0.327184	-0.293715
O	0.798102	-0.602693	0.868047
H	-0.452425	0.974464	1.511529

1b
Electronic Energy = -952.7273614
Enthalpy 298K = -952.616729
Free Energy 298K, 1 atm = -952.664496

O	-2.259515	0.725156	0.806783
C	-0.761845	-0.815449	-0.369286
H	-0.760534	-1.892256	-0.152897
H	-0.696365	-0.701292	-1.456017
C	-2.170865	-0.299953	0.067183
O	-3.125174	-1.014043	-0.394604
C	0.485307	-0.189013	0.248323
C	0.926113	1.193523	-0.376098
O	0.674133	1.343356	-1.606894
O	1.529395	1.982018	0.416197
Cl	1.897701	-1.344861	-0.222949
C	0.459467	-0.183307	1.763235
H	-0.338410	0.500534	2.063589
H	0.233396	-1.190066	2.142182
H	1.416543	0.163508	2.159230

3b‡
Electronic Energy = -952.6994814
Enthalpy 298K = -952.590648
Free Energy 298K, 1 atm = -952.639967
Imaginary Frequency = 313.0i cm^{-1}

C	-0.298222	-0.038453	0.236165
C	-0.948411	-1.008966	-0.690655
C	-0.171493	1.382598	-0.193207
C	-2.464920	-1.380044	-0.427212
H	-0.849092	-0.664292	-1.722381
H	-0.403851	-1.953931	-0.591895
O	-1.404309	1.642899	0.091364
O	0.747303	2.077776	-0.645621
C	-0.313879	-0.302897	1.710437
H	-1.345812	-0.166474	2.048452
H	-0.031628	-1.337853	1.905842
H	0.373479	0.371934	2.228101
Cl	2.104418	-0.973886	0.013750
O	-3.148883	-1.511847	-1.487603
O	-2.808224	-1.595770	0.772466

3b
Electronic Energy = -493.1178842
Enthalpy 298K = -493.010600
Free Energy 298K, 1 atm = -493.055571

C	0.627840	0.547778	-0.033991
C	-0.664796	0.430619	-0.785888
C	1.630169	-0.494332	-0.149102
C	-1.197509	1.719296	-1.513068
H	-0.596782	-0.377317	-1.522611
H	-1.437662	0.128217	-0.063118
O	1.929445	0.503261	-0.983034
O	2.110796	-1.571077	0.156026
O	-0.604774	2.809968	-1.264609
O	-2.194677	1.484365	-2.252286
C	0.750653	1.566463	1.062557
H	0.520691	2.548418	0.642511
H	0.012938	1.332011	1.840343
H	1.750357	1.545373	1.507368

4b‡
Electronic Energy = -952.6947383
Enthalpy 298K = -952.585712
Free Energy 298K, 1 atm = -952.633303
Imaginary Frequency = 482.7i cm^{-1}

C	0.134381	0.005469	0.353048
C	-0.708448	-1.012218	-0.369810
C	0.395720	-0.106472	1.828119
C	-2.080345	-0.451994	-0.031939
H	-0.555958	-2.030677	-0.001125
H	-0.504199	-0.976480	-1.442271
C	0.571152	1.309395	-0.376151
H	0.209445	-1.127167	2.180134
H	1.429377	0.173579	2.028341
H	-0.262324	0.594120	2.348018
O	-1.873452	0.661154	0.602663
O	-3.174253	-0.999816	-0.310977
O	0.302808	1.359374	-1.610228
O	1.115902	2.174469	0.375896
Cl	2.213600	-1.328257	-0.160654

4b
Electronic Energy = -493.1466851
Enthalpy 298K = -493.038579
Free Energy 298K, 1 atm = -493.081875

C	0.219489	0.414521	-0.070467
C	0.539050	1.715609	-0.766769
C	-0.740617	0.486051	1.118685
H	1.257095	2.280906	-0.160777
H	0.991301	1.496297	-1.737625
H	-0.367954	2.317706	-0.907525
C	1.486658	-0.468689	0.099615
C	-1.727325	-0.187035	0.189948
H	-1.044339	1.484355	1.452486
H	-0.415479	-0.121467	1.966262
O	1.978609	-0.897448	-0.980114
O	1.889193	-0.584187	1.298044
O	-2.894521	-0.537683	0.232630
O	-0.869003	-0.297748	-0.864475

1c
Electronic Energy = -991.8928673
Enthalpy 298K = -991.752314
Free Energy 298K, 1 atm = -991.803629

O	1.897023	0.749223	-1.638489
C	0.726840	-0.590899	-0.003028
C	1.861819	0.446525	-0.404576
O	2.668825	0.792493	0.512015
C	-0.626613	-0.013719	-0.448358
C	-1.258344	1.158319	0.380056
O	-1.542796	0.922245	1.592181
O	-1.440771	2.222972	-0.288298
Cl	-1.929721	-1.344844	-0.513562
H	-0.537514	0.305436	-1.487098
C	0.776649	-0.943728	1.481566
H	1.749213	-1.399939	1.705820
H	0.652276	-0.056298	2.101269
H	-0.026196	-1.651522	1.729923
C	1.071414	-1.851734	-0.819819
H	0.446371	-2.702503	-0.520549
H	0.941481	-1.662072	-1.890221
H	2.124480	-2.111023	-0.642885

3c
Electronic Energy = -532.2870963
Enthalpy 298K = -532.149673
Free Energy 298K, 1 atm = -532.196537

C	-0.752869	0.112965	-0.675283
C	0.482254	0.565642	0.043820
C	-1.911907	-0.466436	-0.034667
C	1.171365	1.711111	-0.801185
O	-2.138688	0.825329	-0.295807
H	-0.649581	0.053409	-1.757716
O	-2.521527	-1.382264	0.484497
O	1.093565	1.553512	-2.058400
O	1.762786	2.604198	-0.132810
C	1.441437	-0.640459	0.026259
H	1.030141	-1.482571	0.600030
H	1.638799	-0.963906	-1.001360
H	2.392673	-0.337198	0.478349
C	0.192750	0.986665	1.479289
H	-0.491167	1.839760	1.503938
H	-0.248523	0.160970	2.056382
H	1.127670	1.297644	1.950604

3c‡
Electronic Energy = -991.8667814
Enthalpy 298K = -991.728134
Free Energy 298K, 1 atm = -991.779122
Imaginary Frequency = 295.6i cm^{-1}

C	-1.477346	0.954972	0.011514
C	-0.381064	0.588371	0.957728
C	1.021153	0.800968	0.198211
C	-2.111530	2.289162	0.051272
O	1.896238	1.440451	0.850946
O	1.113609	0.224564	-0.923579
O	-1.123149	2.779043	-0.629203
O	-3.116531	2.797243	0.558613
Cl	-3.460050	-0.628956	0.480491
H	-1.499186	0.433279	-0.936057
C	-0.472413	1.402161	2.245247
H	-0.367576	2.471519	2.039149
H	-1.440905	1.218258	2.729526
H	0.341308	1.113513	2.918132
C	-0.380294	-0.913657	1.294804
H	-1.246876	-1.173446	1.907631
H	-0.407030	-1.510331	0.380063
H	0.549106	-1.134910	1.838313

4c‡
Electronic Energy = -991.8651814
Enthalpy 298K = -991.726244
Free Energy 298K, 1 atm = -991.776467
Imaginary Frequency = 503.5i cm^{-1}

C	0.347056	-0.182989	-0.490984
C	-0.798533	0.639851	0.086523
C	-1.878777	-0.395629	-0.237372
C	1.051864	-1.383298	0.188099
O	-1.300777	-1.291800	-0.981003
O	-3.079488	-0.321137	0.106600
O	0.771281	-1.599571	1.405998
O	1.803910	-2.036423	-0.593610
Cl	2.125195	1.420381	-0.192345
H	0.578060	-0.055409	-1.539871
C	-0.729885	1.004110	1.564853
H	-0.473655	0.121329	2.153533
H	0.035187	1.771578	1.724952
H	-1.714039	1.389412	1.865035
C	-1.089593	1.893640	-0.746883
H	-0.302787	2.637978	-0.593457
H	-1.137656	1.645961	-1.815344
H	-2.061937	2.302458	-0.441614

4c
Electronic Energy = -532.3166404
Enthalpy 298K = -532.177885
Free Energy 298K, 1 atm = -532.223931

C	0.426471	-0.121982	-0.731003
C	-0.712848	0.589071	0.032784
C	1.809236	-0.094486	-0.060008
C	-1.377001	-0.777629	-0.021206
O	2.159310	-1.073217	0.648562
O	2.385992	1.012706	-0.305346
O	-2.447771	-1.246617	0.327081
O	-0.352894	-1.411152	-0.655018
H	0.498846	0.159355	-1.785749
C	-0.379531	1.036335	1.451259
H	0.262382	1.922714	1.413871
H	-1.304555	1.275440	1.990079
H	0.158067	0.251155	1.990707
C	-1.454520	1.669003	-0.742038
H	-1.718564	1.325299	-1.748782
H	-2.377495	1.949888	-0.220482
H	-0.814312	2.554014	-0.832677

1d
Electronic Energy = -1031.0588689
Enthalpy 298K = -1030.889046
Free Energy 298K, 1 atm = -1030.941907

O	-1.633391	1.481293	0.963153
C	-0.793615	-0.576349	-0.071956
C	-1.910986	0.530866	0.173991
O	-3.031704	0.282163	-0.377856
C	0.619230	-0.061578	0.326928
C	1.145360	1.241112	-0.429650
O	0.679047	1.455779	-1.583895
O	2.029337	1.898900	0.199593
Cl	1.883954	-1.376290	-0.183534
C	-0.869357	-1.071455	-1.524310
H	-1.925880	-1.227033	-1.762776
H	-0.443698	-0.325185	-2.197308
H	-0.324989	-2.018710	-1.638984
C	-1.234832	-1.755121	0.824919
H	-0.485230	-2.559571	0.819106
H	-1.412067	-1.438449	1.858842
H	-2.179102	-2.144720	0.427039
C	0.829541	0.067103	1.829756
H	1.835600	0.451499	2.007521
H	0.092211	0.785028	2.198817
H	0.705308	-0.897091	2.336251

3d‡
Electronic Energy = -1031.0302767
Enthalpy 298K = -1030.861900
Free Energy 298K, 1 atm = -1030.915017
Imaginary Frequency = 274.5i cm^{-1}

C	-0.566932	1.193739	-0.013521
C	-0.573572	1.052575	1.497930
C	0.697131	1.147909	-0.820564
C	0.521916	0.050114	2.084773
C	-1.744261	1.809444	-0.666158
H	1.340696	1.986589	-0.528421
H	1.231301	0.226908	-0.598025
H	0.453955	1.208977	-1.885155
O	1.705763	0.229781	1.664927
O	0.116635	-0.708541	3.010427
O	-1.193224	2.971371	-0.426114
O	-2.808846	1.493665	-1.190906
Cl	-1.075071	-1.381688	-0.777798
C	-0.157533	2.402998	2.135876
H	0.818555	2.722390	1.759300
H	-0.900173	3.179273	1.922557
H	-0.080819	2.248592	3.220220
C	-1.980679	0.690317	1.978415
H	-1.972287	0.604983	3.069164
H	-2.702606	1.462171	1.677193
H	-2.281838	-0.269444	1.551296

3d
Electronic Energy = -571.4641505
Enthalpy 298K = -571.297073
Free Energy 298K, 1 atm = -571.347325

C	0.689173	0.245413	0.459153
C	-0.605394	0.457226	-0.294621
C	1.924033	-0.102396	-0.216584
C	-1.617797	-0.633751	0.232732
O	1.887991	1.230023	-0.057735
O	2.709440	-0.899782	-0.686334
O	-2.816301	-0.262564	0.374485
O	-1.091385	-1.774812	0.412935
C	-0.422317	0.212785	-1.796733
H	0.291257	0.925228	-2.232385
H	-0.072876	-0.808838	-1.977147
H	-1.388667	0.342351	-2.297335
C	-1.111255	1.881708	-0.065178
H	-1.304488	2.081945	0.993300
H	-0.384225	2.613223	-0.442830
H	-2.062444	2.001537	-0.590182
C	0.657802	0.176577	1.960509
H	0.070903	1.001378	2.376576
H	0.183169	-0.768993	2.236661
H	1.672973	0.216405	2.367070

4d‡
Electronic Energy = -1031.0328321
Enthalpy 298K = -1030.864142
Free Energy 298K, 1 atm = -1030.916632
Imaginary Frequency = 474.6i cm^{-1}

C	0.289236	-0.215585	-0.440846
C	-0.811667	0.715539	0.095285
C	-1.969810	-0.273902	-0.090052
C	0.839148	-1.432469	0.391362
O	-1.499927	-1.284344	-0.750275
O	-3.147398	-0.058263	0.278675
O	0.453985	-1.517154	1.591838
O	1.580081	-2.216966	-0.270851
Cl	2.206048	1.291309	0.112173
C	-0.693576	1.213878	1.536158
H	-0.343656	0.408409	2.182764
H	0.007758	2.052193	1.589628
H	-1.695295	1.541395	1.847238
C	-1.086852	1.923542	-0.811813
H	-0.207135	2.576818	-0.845024
H	-1.355856	1.619103	-1.829813
H	-1.937088	2.474256	-0.390272
C	0.696963	-0.170535	-1.894448
H	1.680918	-0.630698	-1.979646
H	-0.019825	-0.759426	-2.476703
H	0.733001	0.851779	-2.274794

4d
Electronic Energy = -571.491556
Enthalpy 298K = -571.323285
Free Energy 298K, 1 atm = -571.371774

C	-0.424034	-0.001845	0.520904
C	0.792244	0.526043	-0.291682
C	-1.742863	-0.099165	-0.279700
C	1.426611	-0.790136	0.118268
O	-2.152627	-1.235678	-0.629757
O	-2.228358	1.060629	-0.477212
O	2.529451	-1.303895	0.011830
O	0.316979	-1.313188	0.704252
C	0.562778	0.571952	-1.802660
H	-0.074083	1.427018	-2.049780
H	1.528073	0.665115	-2.316016
H	0.061083	-0.336179	-2.150700
C	1.495053	1.787403	0.185005
H	1.745518	1.750117	1.249176
H	2.427048	1.926126	-0.375983
H	0.845888	2.652696	0.006125
C	-0.659973	0.579122	1.899271
H	-1.057313	1.592729	1.801899
H	-1.402100	-0.037601	2.418473
H	0.259723	0.586776	2.495645

Cl^-
Electronic Energy = -459.6711454
Enthalpy 298K = -459.668785
Free Energy 298K, 1 atm = -459.686168

MP2(fc)/6-31+G(d) : PCM(water)

1a
Electronic Energy = -913.8513206
Enthalpy 298K = -913.769620
Free Energy 298K, 1 atm = -913.815181

O	1.988942	0.633640	-1.080959
C	0.700770	-0.944265	0.199804
H	0.805777	-1.952016	-0.224714
H	0.590787	-1.053284	1.281685
C	1.998342	-0.173673	-0.096304
O	2.993643	-0.440304	0.653321
C	-0.520693	-0.269960	-0.383590
H	-0.467024	-0.216410	-1.470159
C	-0.808421	1.138374	0.180429
O	-0.510691	1.341284	1.397656
O	-1.344480	1.959937	-0.628992
Cl	-1.991367	-1.292228	-0.034948

3a‡
Electronic Energy = -913.8087192
Enthalpy 298K = -913.729347
Free Energy 298K, 1 atm = -913.776029
Imaginary Frequency = 432.8i cm^{-1}

C	1.092158	1.395510	0.027220
O	2.185914	1.744602	-0.417251
C	0.323678	0.168799	0.232569
C	-0.752300	-0.222761	-0.718171
H	-0.586686	-1.261948	-1.019087
H	-0.728402	0.400840	-1.615572
Cl	1.956127	-1.719628	-0.079799
O	0.072344	2.036773	0.512086
C	-2.153325	-0.167653	-0.056462
O	-3.095021	0.272436	-0.785450
O	-2.234593	-0.605819	1.132596
H	0.264585	-0.212050	1.243281

3a
Electronic Energy = -454.0360373
Enthalpy 298K = -453.958187
Free Energy 298K, 1 atm = -453.999820

C	-0.570589	-0.142651	0.564260
C	0.660188	-0.640032	-0.113431
C	-1.841167	-0.011192	-0.112713
C	1.475233	-1.617177	0.765664
H	0.415874	-1.107784	-1.072064
H	1.297097	0.229536	-0.331661
O	-1.786220	-1.165974	0.563176
H	-0.456453	0.302824	1.548802
O	-2.637309	0.558440	-0.828147
O	1.305294	-1.538311	2.021823
O	2.265075	-2.388449	0.138228

4a‡
Electronic Energy = -913.8148578
Enthalpy 298K = -913.735130
Free Energy 298K, 1 atm = -913.779264
Imaginary Frequency = 625.0i cm^{-1}

O	1.643061	0.631201	-0.841387
C	0.718844	-1.050497	0.308325
H	0.675217	-2.075202	-0.070129
H	0.512825	-1.048578	1.380470
C	2.009991	-0.347470	-0.050223
O	3.165095	-0.633056	0.313629
C	-0.166494	-0.101250	-0.448333
H	-0.361606	-0.269862	-1.497486
C	-0.629721	1.218689	0.158818
O	-1.192569	2.022821	-0.647234
O	-0.377390	1.396359	1.389437
Cl	-2.196509	-1.209799	-0.023251

4a
Electronic Energy = -454.0663609
Enthalpy 298K = -453.987458
Free Energy 298K, 1 atm = -454.027413

C	-0.260613	0.392556	0.583286
C	0.676262	1.137905	-0.380646
C	-1.549632	-0.151797	-0.035169
C	1.640993	0.015736	-0.064720
H	1.020588	2.123070	-0.057360
H	0.354445	1.174117	-1.424586
O	-1.558870	-1.335567	-0.479227
O	-2.482271	0.712527	-0.058522
O	2.769148	-0.313287	-0.373308
O	0.803610	-0.636236	0.801160
H	-0.449673	0.899043	1.531172

1b
Electronic Energy = -952.9373701
Enthalpy 298K = -952.825177
Free Energy 298K, 1 atm = -952.872202

O	-2.054344	0.940417	0.582007
C	-0.741833	-0.885883	-0.326088
H	-0.828397	-1.920498	0.030848
H	-0.623796	-0.926883	-1.411865
C	-2.081795	-0.163608	-0.039114
O	-3.105280	-0.766532	-0.480999
C	0.489524	-0.230904	0.267750
C	0.761216	1.182475	-0.340321
O	0.480770	1.315724	-1.565042
O	1.276278	2.035573	0.437251
Cl	1.945951	-1.248057	-0.287517
C	0.505216	-0.263156	1.780897
H	-0.348744	0.320550	2.125580
H	0.411378	-1.291156	2.147018
H	1.423201	0.179793	2.167572

3b‡
Electronic Energy = -952.982384
Enthalpy 298K = -952.873289
Free Energy 298K, 1 atm = -952.922243
Imaginary Frequency = 370.6i cm^{-1}

C	-0.319649	-0.080130	0.266491
C	-0.898609	-1.126907	-0.625583
C	-0.279298	1.309877	-0.226057
C	-2.453932	-1.213954	-0.503356
H	-0.627783	-0.932548	-1.665025
H	-0.494485	-2.096428	-0.322376
O	-1.518663	1.468552	0.105049
O	0.550583	2.057113	-0.753450
C	-0.259873	-0.315099	1.740966
H	-1.288439	-0.335643	2.115366
H	0.186323	-1.289994	1.941816
H	0.311771	0.463839	2.249739
Cl	2.146624	-0.843690	-0.138932
O	-3.105391	-0.949582	-1.559248
O	-2.912705	-1.574611	0.622601

3b
Electronic Energy = -493.2120337
Enthalpy 298K = -493.104470
Free Energy 298K, 1 atm = -493.149383

C	0.618661	0.567538	-0.025246
C	-0.683336	0.430328	-0.758988
C	1.638376	-0.448787	-0.192315
C	-1.143151	1.678533	-1.553235
H	-0.642310	-0.418149	-1.451707
H	-1.458861	0.188522	-0.019939
O	1.887397	0.582203	-1.005477
O	2.152698	-1.520465	0.058765
O	-0.375208	2.686358	-1.585946
O	-2.275957	1.550039	-2.117328
C	0.720213	1.544256	1.107954
H	0.390786	2.530860	0.776772
H	0.064754	1.202586	1.917405
H	1.742627	1.599221	1.490384

4b‡
Electronic Energy = -952.9846722
Enthalpy 298K = -952.875415
Free Energy 298K, 1 atm = -952.922820
Imaginary Frequency = 571.9i cm^{-1}

C	0.151107	-0.075221	0.377654
C	-0.732158	-1.053294	-0.356589
C	0.482255	-0.281695	1.829051
C	-2.044733	-0.357642	-0.070579
H	-0.685749	-2.063315	0.061392
H	-0.511791	-1.092164	-1.424102
C	0.551981	1.233959	-0.326335
H	0.455691	-1.344768	2.082102
H	1.469859	0.120693	2.049099
H	-0.247976	0.247143	2.446949
O	-1.738418	0.690509	0.642689
O	-3.179572	-0.719218	-0.442403
O	0.236695	1.335387	-1.549739
O	1.129165	2.095975	0.404989
Cl	2.205076	-1.169733	-0.375231

4b
Electronic Energy = -493.2427501
Enthalpy 298K = -493.134466
Free Energy 298K, 1 atm = -493.177689

C	0.220883	0.425190	-0.094576
C	0.563282	1.765281	-0.704307
C	-0.746888	0.438627	1.099293
H	1.254935	2.298258	-0.046119
H	1.038401	1.627048	-1.680966
H	-0.343370	2.366079	-0.831555
C	1.454456	-0.475878	0.075447
C	-1.718056	-0.200810	0.134856
H	-1.054479	1.425449	1.457934
H	-0.466585	-0.196665	1.943234
O	1.603006	-1.449980	-0.717883
O	2.223867	-0.096864	1.013781
O	-2.870219	-0.593271	0.147284
O	-0.857076	-0.231274	-0.926504

1c
Electronic Energy = -992.1870502
Enthalpy 298K = -992.045923
Free Energy 298K, 1 atm = -992.096427

O	1.564916	1.194485	-1.270770
C	0.710743	-0.634035	0.040497
C	1.745046	0.500927	-0.214722
O	2.716610	0.617357	0.596607
C	-0.648327	-0.086132	-0.417488
C	-1.091066	1.291202	0.136163
O	-0.683782	1.630700	1.288378
O	-1.860153	1.955345	-0.631232
Cl	-2.008289	-1.250837	-0.041067
H	-0.656757	-0.020929	-1.505057
C	0.736912	-1.113261	1.490292
H	1.752795	-1.425281	1.746818
H	0.429649	-0.316222	2.169265
H	0.069484	-1.971703	1.622510
C	1.115531	-1.804668	-0.873897
H	0.425463	-2.647536	-0.751509
H	1.113403	-1.498454	-1.925559
H	2.122258	-2.152023	-0.613283

3c
Electronic Energy = -532.3770803
Enthalpy 298K = -532.239492
Free Energy 298K, 1 atm = -532.286691

C	-0.725729	0.033028	-0.678348
C	0.492992	0.535424	0.040005
C	-1.955619	-0.344491	-0.019056
C	1.099542	1.719041	-0.777123
O	-2.050638	0.897926	-0.511254
H	-0.595005	-0.244337	-1.721473
O	-2.668836	-1.103439	0.603011
O	0.909919	1.691739	-2.035382
O	1.768944	2.576481	-0.124634
C	1.510533	-0.622629	0.015133
H	1.121478	-1.490268	0.561128
H	1.742300	-0.926404	-1.011033
H	2.436316	-0.296933	0.500648
C	0.185358	0.929036	1.482877
H	-0.538380	1.748979	1.528006
H	-0.216407	0.074036	2.040635
H	1.102409	1.261184	1.972802

3c‡
Electronic Energy = -992.1462642
Enthalpy 298K = -992.007368
Free Energy 298K, 1 atm = -992.058157
Imaginary Frequency = 364.5i cm^{-1}

C	-1.453485	0.952528	0.000104
C	-0.377465	0.574877	0.967955
C	0.983284	0.851475	0.208096
C	-2.061763	2.285188	0.014722
O	1.821634	1.593886	0.797299
O	1.120756	0.255847	-0.904294
O	-1.029314	2.696920	-0.656859
O	-3.054154	2.854027	0.471020
Cl	-3.506655	-0.504336	0.597461
H	-1.522819	0.394174	-0.924877
C	-0.498390	1.363649	2.267481
H	-0.431966	2.441654	2.095592
H	-1.456878	1.136175	2.748771
H	0.309576	1.084229	2.948645
C	-0.362339	-0.933267	1.274835
H	-1.203864	-1.201694	1.915523
H	-0.412365	-1.522962	0.356656
H	0.573673	-1.170168	1.794671

4c‡
Electronic Energy = -992.153885
Enthalpy 298K = -992.014385
Free Energy 298K, 1 atm = -992.064216
Imaginary Frequency = 604.2i cm^{-1}

C	0.350741	-0.151126	-0.505622
C	-0.792907	0.658398	0.095809
C	-1.824118	-0.419268	-0.200310
C	0.992766	-1.389037	0.124579
O	-1.229475	-1.243071	-1.027269
O	-2.993435	-0.484371	0.220557
O	0.663261	-1.682073	1.314052
O	1.772557	-2.033210	-0.644807
Cl	2.180827	1.238070	0.024182
H	0.613564	0.038462	-1.538035
C	-0.725751	1.064621	1.561610
H	-0.419798	0.225123	2.186852
H	-0.022029	1.889946	1.696415
H	-1.722801	1.400957	1.868071
C	-1.112689	1.882756	-0.771977
H	-0.318598	2.628369	-0.670691
H	-1.208964	1.607533	-1.828283
H	-2.057727	2.328360	-0.442022

4c
Electronic Energy = -532.4118112
Enthalpy 298K = -532.272936
Free Energy 298K, 1 atm = -532.318781

C	0.430005	-0.100657	-0.738651
C	-0.711119	0.604013	0.038152
C	1.806113	-0.135522	-0.076983
C	-1.355645	-0.769497	-0.008549
O	2.148243	-1.159885	0.580587
O	2.455228	0.942804	-0.261979
O	-2.395834	-1.278272	0.365240
O	-0.333125	-1.386888	-0.676772
H	0.507642	0.200659	-1.786633
C	-0.393329	1.063765	1.456736
H	0.219910	1.969608	1.424136
H	-1.325298	1.292542	1.984303
H	0.145666	0.295090	2.018533
C	-1.469700	1.666615	-0.747725
H	-1.722220	1.316115	-1.753720
H	-2.395698	1.934090	-0.228060
H	-0.850026	2.565319	-0.836583

1d
Electronic Energy = -1031.2647983
Enthalpy 298K = -1031.092537
Free Energy 298K, 1 atm = -1031.143786

O	-1.544418	1.492104	0.924531
C	-0.782865	-0.590626	-0.077261
C	-1.820559	0.574852	0.092263
O	-2.900606	0.461089	-0.560482
C	0.619967	-0.071514	0.321912
C	1.020670	1.281436	-0.375598
O	0.511089	1.523302	-1.506648
O	1.860651	1.992450	0.246933
Cl	1.918326	-1.266568	-0.297696
C	-0.846521	-1.143069	-1.504423
H	-1.896559	-1.296452	-1.756871
H	-0.407511	-0.433489	-2.203267
H	-0.319998	-2.099248	-1.579119
C	-1.263686	-1.712006	0.859835
H	-0.554142	-2.547852	0.875728
H	-1.410227	-1.359790	1.884464
H	-2.224740	-2.085504	0.492324
C	0.862614	-0.014891	1.821758
H	1.845245	0.417148	2.006171
H	0.096812	0.627963	2.255228
H	0.811195	-1.007143	2.275866

3d‡
Electronic Energy = -1031.3182288
Enthalpy 298K = -1031.149618
Free Energy 298K, 1 atm = -1031.202096
Imaginary Frequency = 334.6i cm^{-1}

C	-0.562367	1.159655	-0.011272
C	-0.582415	1.040376	1.495341
C	0.707883	1.283906	-0.794369
C	0.409932	-0.059986	2.033708
C	-1.779988	1.669896	-0.682897
H	1.195500	2.230165	-0.532476
H	1.387714	0.480192	-0.520672
H	0.498958	1.274131	-1.866540
O	1.620093	0.032840	1.662291
O	-0.065061	-0.876393	2.879352
O	-1.440767	2.888360	-0.413637
O	-2.752598	1.194070	-1.276434
Cl	-0.851161	-1.385080	-0.646732
C	-0.054312	2.357887	2.122815
H	0.947739	2.597281	1.759707
H	-0.732947	3.183576	1.893759
H	-0.007186	2.223136	3.209681
C	-2.008850	0.799058	1.990576
H	-2.011888	0.739658	3.081393
H	-2.662922	1.626052	1.690951
H	-2.407243	-0.136658	1.590872

3d
Electronic Energy = -571.5552376
Enthalpy 298K = -571.387969
Free Energy 298K, 1 atm = -571.437740

C	0.692366	0.226084	0.455744
C	-0.606517	0.428540	-0.295204
C	1.859600	-0.321115	-0.198281
C	-1.533933	-0.756014	0.118456
O	1.950610	1.013583	-0.211171
O	2.543128	-1.247900	-0.585746
O	-2.782056	-0.536626	0.132863
O	-0.941436	-1.857788	0.358783
C	-0.405061	0.334606	-1.814127
H	0.235476	1.147963	-2.172360
H	0.042967	-0.622936	-2.101358
H	-1.377307	0.420607	-2.309891
C	-1.204119	1.792626	0.055404
H	-1.496284	1.854360	1.107530
H	-0.478106	2.587248	-0.157948
H	-2.097387	1.966235	-0.549640
C	0.705927	0.394303	1.949711
H	0.563923	1.447711	2.209413
H	-0.112229	-0.186332	2.385146
H	1.650030	0.049506	2.379034

4d‡
Electronic Energy = -1031.3198592
Enthalpy 298K = -1031.150707
Free Energy 298K, 1 atm = -1031.202329
Imaginary Frequency = 547.9i cm^{-1}

C	0.288508	-0.210034	-0.458585
C	-0.805314	0.717916	0.100134
C	-1.913871	-0.319946	-0.022550
C	0.763643	-1.441700	0.354628
O	-1.446431	-1.270426	-0.781279
O	-3.057244	-0.237133	0.470342
O	0.322819	-1.556526	1.537441
O	1.519189	-2.250049	-0.266401
Cl	2.251594	1.041110	0.297667
C	-0.669677	1.283575	1.512773
H	-0.270032	0.540998	2.201813
H	-0.022747	2.163788	1.510874
H	-1.671574	1.583924	1.841827
C	-1.133334	1.878744	-0.850786
H	-0.280185	2.562503	-0.919974
H	-1.398017	1.534793	-1.855102
H	-1.986204	2.432780	-0.443740
C	0.729015	-0.099226	-1.895782
H	1.660693	-0.645939	-2.030943
H	-0.034626	-0.540963	-2.542903
H	0.872848	0.940688	-2.188868

4d
Electronic Energy = -571.5862139
Enthalpy 298K = -571.417917
Free Energy 298K, 1 atm = -571.466791

C	-0.424261	0.006726	0.534843
C	0.787568	0.530373	-0.298999
C	-1.726069	-0.184119	-0.259285
C	1.409152	-0.796197	0.086985
O	-2.071808	-1.354698	-0.594525
O	-2.326650	0.911888	-0.493472
O	2.479696	-1.356394	-0.074479
O	0.320820	-1.289107	0.746198
C	0.561106	0.619798	-1.808388
H	-0.031166	1.509401	-2.042008
H	1.528649	0.697913	-2.315964
H	0.037991	-0.260930	-2.193137
C	1.523088	1.763918	0.208448
H	1.790728	1.689529	1.265237
H	2.444740	1.901869	-0.366874
H	0.894867	2.650105	0.066167
C	-0.682639	0.629031	1.890593
H	-1.051269	1.650272	1.767489
H	-1.442931	0.046285	2.421959
H	0.227486	0.642375	2.496570

Cl^-
Electronic Energy = -459.7819089
Enthalpy 298K = -459.779548
Free Energy 298K, 1 atm = -459.796932

B3LYP/6-31+G(d) : PCM(water)

1a

SCF (B3LYP) Energy = -915.6823847
Enthalpy 298K = -915.601886
Free Energy 298K, 1 atm = -915.648158

O	2.050390	0.622451	-1.079879
C	0.714076	-0.918394	0.217282
H	0.789737	-1.946770	-0.160513
H	0.612964	-0.977957	1.304430
C	2.049369	-0.206919	-0.125117
O	3.048263	-0.547244	0.573414
C	-0.505024	-0.243416	-0.382539
H	-0.446677	-0.186948	-1.467305
C	-0.866731	1.155235	0.198053
O	-0.614579	1.353957	1.417247
O	-1.395832	1.964889	-0.614628
Cl	-2.000711	-1.338811	-0.087760

1b

SCF (B3LYP) Energy = -954.9225154
Enthalpy 298K = -954.812613
Free Energy 298K, 1 atm = -954.860419

O	-2.127585	0.900537	0.619438
C	-0.755595	-0.875828	-0.332981
H	-0.829871	-1.919079	-0.000804
H	-0.642354	-0.886626	-1.420340
C	-2.126889	-0.181321	-0.027103
O	-3.126182	-0.795219	-0.486248
C	0.470743	-0.213896	0.272686
C	0.802634	1.195408	-0.354935
O	0.539302	1.329043	-1.576269
O	1.316589	2.037964	0.423725
Cl	1.986469	-1.309484	-0.291937
C	0.508712	-0.253027	1.788272
H	-0.350447	0.324583	2.140903
H	0.421836	-1.279217	2.163453
H	1.422789	0.203936	2.170490

1c

SCF (B3LYP) Energy = -994.3015971
Enthalpy 298K = -994.162574
Free Energy 298K, 1 atm = -994.214310

O	-1.611110	-1.212654	-1.271846
C	-0.725020	0.626438	0.035514
C	-1.794834	-0.500130	-0.240310
O	-2.779970	-0.578418	0.544414
C	0.638525	0.062741	-0.422214
C	1.145853	-1.292741	0.165299
O	0.827740	-1.591842	1.347258
O	1.860921	-1.976556	-0.622446
Cl	2.029882	1.296780	-0.103159
H	0.653137	-0.017902	-1.506067
C	-0.750784	1.091711	1.499504
H	-1.754632	1.441808	1.756235
H	-0.478253	0.278117	2.174275
H	-0.049650	1.920591	1.651798
H	-1.115128	1.819121	-0.873154
H	-0.416118	2.653720	-0.743697
H	-1.116557	1.532615	-1.931167
H	-2.118232	2.178709	-0.614543

1d

SCF (B3LYP) Energy = -1033.5376118
Enthalpy 298K = -1033.368771
Free Energy 298K, 1 atm = -1033.421224

O	-1.559049	1.564881	0.840173
C	-0.796289	-0.590599	-0.067201
C	-1.878268	0.564123	0.142587
O	-3.006074	0.345283	-0.372379
C	0.605179	-0.052662	0.337438
C	1.106641	1.257168	-0.414135
O	0.701156	1.448155	-1.588649
O	1.903517	1.980948	0.235051
Cl	1.961800	-1.370063	-0.234783
C	-0.874067	-1.089478	-1.524025
H	-1.926063	-1.251818	-1.770648
H	-0.450012	-0.346125	-2.198884
H	-0.332389	-2.033691	-1.649516
C	-1.250022	-1.760483	0.839555
H	-0.527572	-2.585892	0.815006
H	-1.386765	-1.458552	1.883315
H	-2.211820	-2.136773	0.476797
C	0.839740	0.033053	1.839289
H	1.818779	0.471075	2.031290
H	0.070542	0.696377	2.243952
H	0.767695	-0.941761	2.328533

B3LYP/6-31+G(d) : PCM(water), empiricaldispersion=GD3BJ

1a
SCF (B3LYP) Energy = -915.8534811
Enthalpy 298K = -915.773307
Free Energy 298K, 1 atm = -915.819365

O	2.029679	0.581604	-1.094017
C	0.694543	-0.943092	0.202441
H	0.765170	-1.962760	-0.190491
H	0.592495	-1.012014	1.285462
C	2.028053	-0.230118	-0.131738
O	3.015691	-0.551079	0.580551
C	-0.509245	-0.246216	-0.387419
H	-0.462941	-0.191417	-1.469555
C	-0.825321	1.157522	0.198369
O	-0.534933	1.346673	1.404099
O	-1.355277	1.972707	-0.598417
Cl	-2.027305	-1.297742	-0.073709

1b
SCF (B3LYP) Energy = -955.1835897
Enthalpy 298K = -955.074672
Free Energy 298K, 1 atm = -955.122565

O	-2.111561	0.893463	0.595475
C	-0.748295	-0.887795	-0.326239
H	-0.809291	-1.922267	0.022377
H	-0.653616	-0.915183	-1.412027
C	-2.106260	-0.205138	-0.013094
O	-3.117314	-0.837380	-0.425379
C	0.486037	-0.223512	0.264449
C	0.798194	1.186683	-0.351322
O	0.518941	1.335970	-1.565232
O	1.321182	2.029359	0.417439
Cl	1.963682	-1.285633	-0.327436
C	0.533572	-0.277039	1.778142
H	-0.290118	0.327352	2.160404
H	0.408202	-1.304734	2.128166
H	1.470525	0.125629	2.158301

1c
SCF (B3LYP) Energy = -994.5078045
Enthalpy 298K = -994.369441
Free Energy 298K, 1 atm = -994.421330

O	-1.564330	-1.247836	-1.234519
C	-0.715309	0.639358	0.006831
C	-1.784494	-0.484760	-0.255107
O	-2.797952	-0.505388	0.486000
C	0.640746	0.064707	-0.430225
C	1.128011	-1.279330	0.187420
O	0.755677	-1.566786	1.349726
O	1.878703	-1.960425	-0.558696
Cl	2.026584	1.295524	-0.110180
H	0.667777	-0.031922	-1.509243
C	-0.743296	1.125762	1.459235
H	-1.751501	1.455366	1.710753
H	-0.450516	0.327184	2.138130
H	-0.059594	1.967894	1.592481
C	-1.094539	1.812141	-0.922875
H	-0.385523	2.636781	-0.814108
H	-1.101855	1.499487	-1.970144
H	-2.089626	2.185255	-0.667729

1d
SCF (B3LYP) Energy = -1033.8311229
Enthalpy 298K = -1033.663889
Free Energy 298K, 1 atm = -1033.716275

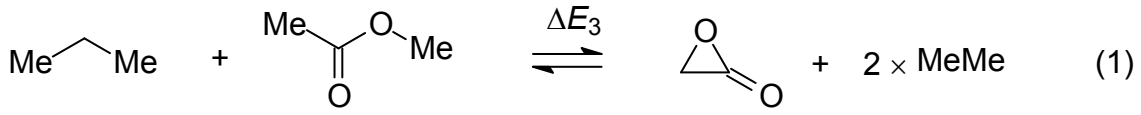
O	-1.542528	1.477481	0.960750
C	-0.783746	-0.611415	-0.036201
C	-1.837189	0.549651	0.163221
O	-2.932134	0.423976	-0.443840
C	0.633343	-0.069255	0.323233
C	1.041119	1.264218	-0.421631
O	0.522687	1.480479	-1.542373
O	1.881252	1.988961	0.166802
Cl	1.947077	-1.313813	-0.338487
C	-0.881915	-1.178745	-1.463101
H	-1.932074	-1.359707	-1.688997
H	-0.476062	-0.477427	-2.188117
H	-0.339875	-2.123230	-1.538393
C	-1.214443	-1.739084	0.929037
H	-0.478278	-2.548047	0.930042
H	-1.342372	-1.387063	1.953664
H	-2.168328	-2.149878	0.592056
C	0.932207	-0.012002	1.813483
H	1.925429	0.399572	1.975204
H	0.195827	0.642837	2.278954
H	0.872657	-0.999442	2.270764

MP2(fc)/6-311+G(d,p) electronic energies (/hartrees) for MP2/6-31+G(d) optimised structures.

structure	PCM	vacuum
1a	-914.096919	-913.794809
3a‡	-914.052473	-913.770409
3a	-914.057986	-913.764168
4a‡	-454.245677	-454.152319
4a	-454.276438	-454.180026
1b	-953.297038	-952.999599
3b‡	-953.254422	-952.969484
3b	-953.256301	-952.964136
4b‡	-493.449497	-493.354870
4b	-493.480529	-493.384568
1c	-992.490942	-992.192412
3c‡	-992.448364	-992.168382
3c	-992.455373	-992.164853
4c‡	-532.643872	-532.553175
4c	-532.678561	-532.583438
1d	-1031.684562	-1031.391218
3d‡	-1031.648134	-1031.359295
3d	-1031.650045	-1031.361085
4d‡	-571.8499814	-571.7580922
4d	-571.8810943	-571.7864393
Cl^-	-459.8149242	-459.7035702

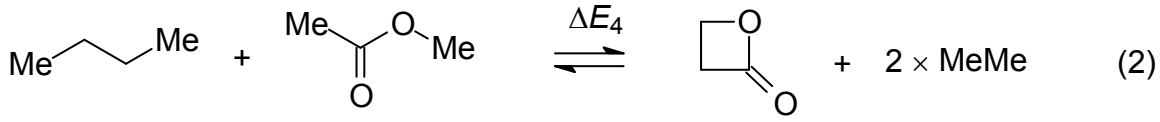
Evaluation of ring-strain energies for α- and β-lactones

In earlier work, the conventional ring-strain energy of oxiranone, the parent unsubstituted α-lactone, was estimated by means of the following isodesmic relation.[1]



(1)

A similar isodesmic relation may be used to estimate the conventional ring-strain energy of oxetanone, the parent unsubstituted β-lactone,



(2)

The necessary energies (in hartrees) for MP2/6-31+G(d) optimised structures in vacuum and MP2/6-311+G(d,p) single-point energies evaluated for these geometries are tabulated below.

	MP2/6-31+G(d)	MP2/6-311+G(d,p)//MP2/6-31+G(d)
ethane	-79.49760	-79.57148
propane	-118.66488	-118.76707
butane	-157.83213	-157.96265
methyl acetate	-267.59069	-267.74473
oxiranone	-227.19009	-227.30051
oxetanone	-266.39069	-266.52855

The ring-strain energies ΔE_3 and ΔE_4 (in kJ mol^{-1}) derived by substitution of these energies into equations (1) and (2), respectively, are given below.

	MP2/6-31+G(d)	MP2/6-311+G(d,p)//MP2/6-31+G(d)
ΔE_3	184	179
ΔE_4	97	94

The key result is that **the ring-strain energy of the simplest α-lactone is about 85 – 87 kJ mol^{-1} larger than of the simplest β-lactone**. (The basis-set effect is quite small.)

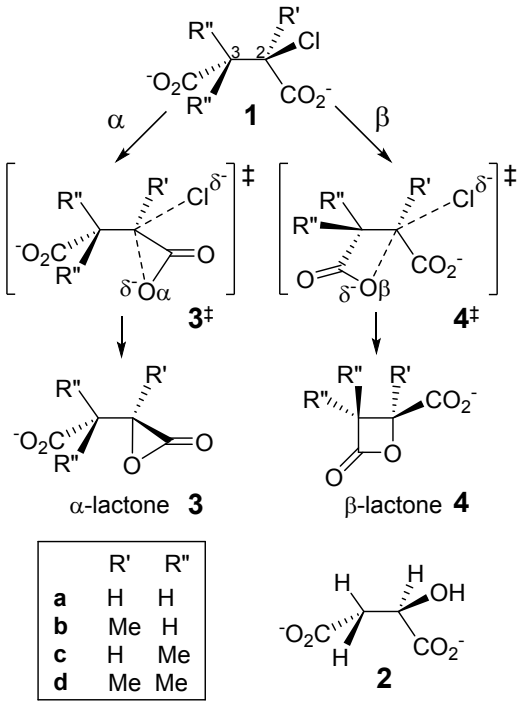
[1] Ring strain energy and enthalpy of formation of oxiranone: an *ab initio* theoretical determination.
C. F. Rodriquez and I. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 953 – 957.

Comparison of B3LYP/6-31+G(d) and MP2/6-31+G(d) results for competing reactions of 1a

In earlier work, the relative barrier heights for formation of α-lactone **3a** or β-lactone **4a** from succinate dianion **1a** was estimated by means of B3LYP/6-31+G* calculations in PCM water.[2] These quantities are simply the energies of **3a**‡ and **4a**‡ relative to the energy of **1a**.

In the present study it has been demonstrated that the stabilities of **1b**, **1c** and **1d** relative to **1a** is predicted to be in the completely the wrong order by B3LYP with either the 6-31+G(d) basis or the larger 6-311+G(d,p) basis. This finding raises a question of doubt in regard to the validity of the results from our 2006 study.

The 2006 results are compared with the present MP2 calculated barrier heights and reaction energies (in kJ mol^{-1}) in the Table below.



	R'	R"
a	H	H
b	Me	H
c	H	Me
d	Me	Me

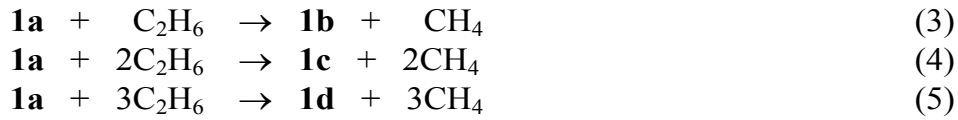
	$\Delta E^{\ddagger}$		ΔE_{rxn}	
method	3	4	3	4
B3LYP/6-31+G*	108	85	64	-22
MP2/6-31+G(d)	112	96	88	8

Both methods predict a higher barrier for α-lactone formation than for β-lactone formation, although the difference in $\Delta E^{\ddagger}$ is larger for B3LYP than for MP2. Both methods also predict that the reaction energy ΔE_{rxn} is more exothermic for 4MR than for 3MR formation, in accord with the relative ring-strain energies of simple α- and β-lactones. Thus the key findings reported in the 2006 paper remain valid although, as commented in the present paper, this is fortuitous. (We were lucky!) The standard B3LYP method without dispersion corrections would not give reliable results for the relative barrier heights for competing intramolecular ring-closure reactions of methyl-substituted succinates.

[2] The Walden cycle revisited: a computational study of competitive ring closure to α- and β-lactones. J. G. Buchanan, R. A. Diggle, G. D. Ruggiero and I. H. Williams, *Chem. Commun.*, **2006**, 1106 - 1108.

Comment on alternative isodesmic schemes

Isodesmic schemes are presented in the paper in order to evaluate the stabilities of **1b**, **1c** and **1d** relative to **1a** by means of equations (3 – 5) below.

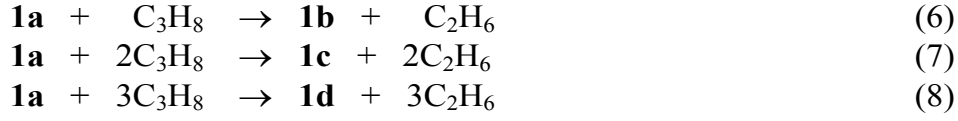


$$\mathbf{1a} + C_2H_6 \rightarrow \mathbf{1b} + CH_4 \quad (3)$$

$$\mathbf{1a} + 2C_2H_6 \rightarrow \mathbf{1c} + 2CH_4 \quad (4)$$

$$\mathbf{1a} + 3C_2H_6 \rightarrow \mathbf{1d} + 3CH_4 \quad (5)$$

Alternatively, so-called "end effects" might be reduced by replacing ethane with propane and ethane with methane, as in equations (6 – 8).



$$\mathbf{1a} + C_3H_8 \rightarrow \mathbf{1b} + C_2H_6 \quad (6)$$

$$\mathbf{1a} + 2C_3H_8 \rightarrow \mathbf{1c} + 2C_2H_6 \quad (7)$$

$$\mathbf{1a} + 3C_3H_8 \rightarrow \mathbf{1d} + 3C_2H_6 \quad (8)$$

However, taking the difference between equations (3) and (6) yields:

$$CH_4 + C_3H_8 \rightarrow 2C_2H_6 \quad (9)$$

The MP2/6-311+G(d,p) energy for equation (9) in PCM water is 9.727 kJ mol^{-1}.

Similarly, the differences between equations (4) and (7) and between (5) and (8) yield multiples of this energy difference, *viz*. 19.454 and 29.181 kJ mol^{-1}, respectively. If more quantitative evaluations of the relative stabilities were required, the results presented in Table 2 of the paper could be corrected by these amounts. This was not done in the paper as the purpose of the isodesmic schemes was to demonstrate the qualitative unreliability of the standard B3LYP method.