Meyer–Schuster-type Rearrangement for the Synthesis of α-Selanyl-α,β-Unsaturated Thioesters

Lucas L. Baldassari,[§] Anderson C. Mantovani,[§] Micaela Jardim,[§] Boris Maryasin,*[,†,‡] and Diogo S. Lüdtke*[,§]

[§] *Instituto de Química, Universidade Federal do Rio Grande do Sul, UFRGS, Av. Bento Gonçalves 9500, 91501-970, Porto Alegre, RS, Brazil.*

[†] *Institute of Organic Chemistry, University of Vienna, WähringerStraße 38, 1090 Vienna, Austria.*

[‡] *Institute of Theoretical Chemistry, University of Vienna, WähringerStraße 17, 1090 Vienna, Austria*

* E-mail: dsludtke@iq.ufrgs.br
* E-mail: boris.maryasin@univie.ac.at

Supporting Information - Computational details

The conformational space of all molecules has been initially searched using the OPLS_2005 force field[1] and the systematic Monte Carlo conformers search routine implemented in MACROMODEL11.5.[2]

Accordingly, the structures located at force field level have then been subjected toB3LYP-D3/def2-SVP[3–8](using def2-ECP[9] for iodine atom) geometry optimization. The nature of all stationary points (minima and transition states) was verified through the computation of the vibrational frequencies. The thermal corrections to the Gibbs free energy were combined with the single point energies calculated at the DLPNO-CCSD(T)/def2-TZVP[10,11] to yieldGibbs free energies ("G_{298}") at 298.15 K.All energies are reported in kcal mol^{-1}.

The density-based solvation model SMD[12] was applied to consider solvent (DCM) effects for both geometries and energies. Solvation factors (for the Gibbs free energies at the DLPNO-CCSD(T)//DFT level of theory) have been calculated by single point energies in gas phase of the optimized geometries in solution. Free energies in solution have been corrected to a reference state of 1 mol l^{-1} at 298.15 K through addition of RTln(24.46) = +7.925 kJ mol^{-1} to the gas phase (1 atm) free energies.

The DFT calculations have been performed with the Gaussian16 program package.[13]The ORCA 4.0.1 software was applied for the DLPNO-CCSD(T) computations.[14]

References

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Coordinates of the most stable ($\Delta G_{298,DCM}$) conformations as computed at the DLPNO-CCSD(T)/def2-TZVP//B3LYP-D3/def2-SVP level of theory

A
C 0.32973 -0.15373 0.00778
C -0.87594 -0.34333 -0.01184
S -2.53692 -0.67387 -0.04489
C -3.24570 1.01761 0.04022
H -2.92906 1.61130 -0.82917
H -4.33821 0.88789 0.02217
H -2.94669 1.51315 0.97485
C 1.79442 0.05888 0.03357
C 2.50013 -1.15282 -0.60079
H 2.25364 -2.07464 -0.04952
H 3.58915 -0.99736 -0.55433
H 2.20075 -1.28780 -1.65140
C 2.15042 1.35436 -0.70600
H 3.23936 1.50940 -0.65555
H 1.84292 1.30359 -1.76054
H 1.65309 2.21181 -0.22817
O 2.25751 0.24690 1.37453
H 2.04721 -0.55648 1.87599

PhSeI
Se 0.25107 1.34710 -0.05648

C -1.41604 0.38432 -0.01862
C -2.00872 -0.03734 -1.22064
C -2.05749 0.14641 1.20833
C -3.24190 -0.69381 -1.19098
H -1.50405 0.14598 -2.17192
C -3.29206 -0.50866 1.22804
H -1.59038 0.47107 2.14085
C -3.88343 -0.92945 0.03106
H -3.70340 -1.02263 -2.12575
H -3.79267 -0.69262 2.18223
H -4.84766 -1.44409 0.05042
I 1.93018 -0.63072 0.03059

A'
C -2.56392 -1.23076 0.23036
C -2.72438 -0.24920 0.93935
S -2.92850 1.09027 1.95479
C -3.37371 2.39042 0.73908
H -2.56440 2.51778 0.00891
H -3.49847 3.31622 1.32014
H -4.31706 2.13819 0.23436
Se 0.67037 -0.37715 0.64246
C 0.19050 1.21557 -0.33492
C 0.43017 2.47640 0.23373
C -0.43342 1.10669 -1.58782
C 0.06108 3.62969 -0.46360
H 0.90538 2.55327 1.21411
C -0.80405 2.26695 -2.27440
H -0.64899 0.12286 -2.00837
C -0.55212 3.52643 -1.71838
H 0.24897 4.61226 -0.02308
H -1.29333 2.18378 -3.24826
H -0.84076 4.43059 -2.26068
C -2.33935 -2.41863 -0.62697
C -2.05144 -3.63794 0.26716
H -1.86169 -4.51305 -0.37334
H -2.90031 -3.85731 0.93285
H -1.15942 -3.45708 0.88757
C -3.55861 -2.66495 -1.52315
H -3.74785 -1.78587 -2.15742
H -4.45520 -2.87003 -0.92015
H -3.35774 -3.53005 -2.17404
O -1.24169 -2.20409 -1.52078
H -0.46493 -1.95880 -0.98430
I 3.21261 -0.47840 0.10029

TS_{A-B}
C 1.79721 1.15323 -0.17059
C 2.56781 0.16014 -0.27616
S 3.44246 -1.20751 -0.49677
C 3.75269 -1.79914 1.21645
H 2.79244 -1.95512 1.72427
H 4.28570 -2.75453 1.10626
H 4.37759 -1.07109 1.75104
Se -0.38181 0.61135 -0.08786
C -0.10465 -1.30510 -0.09781
C 0.02837 -1.99818 1.11399
C -0.02872 -1.99490 -1.31595
C 0.24179 -3.38023 1.10349
H -0.03623 -1.45780 2.06105
C 0.18513 -3.37704 -1.31951
H -0.13556 -1.45209 -2.25778
C 0.32190 -4.07007 -0.11188
H 0.34519 -3.91925 2.04896
H 0.24509 -3.91306 -2.27039
H 0.48870 -5.15045 -0.11713
C 1.91995 2.66933 -0.00911
C 2.13110 2.96373 1.47914
H 2.19695 4.05399 1.61672
H 3.05561 2.49488 1.84473
H 1.28022 2.58607 2.06465
C 3.08884 3.17146 -0.86604
H 2.91423 2.94336 -1.92978
H 3.17829 4.26230 -0.74865
H 4.03379 2.69720 -0.56119
O 0.72071 3.32838 -0.36985
H 0.60172 3.25478 -1.33076
I -3.26219 0.34205 0.08333

B
C 1.47530 1.07592 0.04498
C 1.32459 1.06006 -1.23327
S 1.14812 1.13242 -2.84628
C -0.35275 0.11647 -3.16977
H -0.10951 -0.93869 -2.98976
H -1.16842 0.45350 -2.51414
H -0.58616 0.29233 -4.22950
Se 2.50780 -0.58851 0.30746
C 1.05359 -1.85347 0.38301
C 0.89626 -2.75949 -0.67673
C 0.19841 -1.88477 1.49327
C -0.13442 -3.70165 -0.62209
H 1.56698 -2.72441 -1.53826
C -0.83207 -2.82777 1.53161
H 0.31940 -1.15863 2.29763
C -0.99838 -3.73403 0.47919
H -0.26620 -4.40832 -1.44539
H -1.51367 -2.84556 2.38526

H -1.80946 -4.46580 0.51365
C 1.01402 2.01623 1.17471
C 2.23021 2.43003 2.00129
H 1.88672 3.08663 2.81484
H 2.71410 1.54913 2.44839
H 2.96330 2.97387 1.38729
C 0.31225 3.23069 0.55736
H 1.00375 3.80277 -0.07988
H -0.55415 2.91722 -0.04357
H -0.04532 3.88193 1.36879
O 0.16353 1.28723 2.02626
H -0.67765 1.09838 1.55384
I -2.75074 0.54847 0.09747

TS_{B-C}
C -0.53991 1.18697 0.26944
C -0.25850 0.04925 0.89805
S -0.50586 -1.41165 1.57297
C 0.18077 -2.60734 0.35564
H -0.03377 -3.60250 0.77159
H -0.32841 -2.46974 -0.60706
H 1.26439 -2.44507 0.26476
Se -2.08850 1.66948 -0.69836
C -3.05811 0.00638 -0.47040
C -3.96922 -0.12549 0.58501
C -2.82804 -1.05266 -1.35874
C -4.64534 -1.33769 0.75819
H -4.14047 0.70508 1.27330
C -3.50713 -2.26134 -1.17422
H -2.11749 -0.93863 -2.18048
C -4.41208 -2.40460 -0.11646
H -5.35398 -1.44780 1.58301
H -3.32616 -3.09258 -1.86039
H -4.93971 -3.35127 0.02534
C 0.68163 2.05357 0.48669
C 1.41003 2.40949 -0.80032
H 1.59146 1.51770 -1.41642
H 2.37743 2.87654 -0.56031
H 0.80546 3.12593 -1.37655
C 0.39937 3.26290 1.36622
H -0.08290 2.95312 2.30490
H -0.26156 3.96870 0.84101
H 1.34770 3.76954 1.60157
O 1.41867 1.06938 1.29764
H 2.15198 0.63877 0.77345
I 3.81280 -0.75501 -0.34032

C
C -0.61931 0.46014 -0.26064
C 0.50078 1.07871 0.14717
S 1.33414 2.57964 -0.02228
C 1.85286 2.85443 1.71696
H 0.97562 2.90883 2.37684
H 2.54021 2.06003 2.03946
H 2.38336 3.81749 1.71977
Se -2.09035 0.98387 -1.31604
C -3.46070 0.04705 -0.30434
C -4.07941 -1.07926 -0.86196
C -3.83088 0.50611 0.96744
C -5.06788 -1.75418 -0.13599
H -3.78535 -1.43414 -1.85247
C -4.81168 -0.18025 1.68962
H -3.34950 1.38885 1.39461
C -5.43032 -1.30938 1.13969
H -5.55021 -2.63425 -0.56929
H -5.09600 0.17176 2.68472
H -6.19852 -1.84188 1.70632
C -0.18404 -0.88206 0.30965
C -0.91613 -1.41306 1.51288
H -1.14056 -0.61145 2.22918
H -0.31741 -2.19581 2.00248
H -1.86392 -1.85717 1.17359
C 0.25409 -1.91559 -0.69618
H 0.79532 -2.73924 -0.20871
H 0.87998 -1.47473 -1.48377
H -0.65990 -2.31938 -1.16029
O 1.08170 -0.07007 0.84122
I 4.04089 -0.85860 -0.10410
H 2.04741 -0.37439 0.49133

TS_{C-D}
C 0.60291 1.03182 0.54379
C -0.60377 1.47011 0.13770
S -1.27278 2.36011 -1.19902
C -0.43472 1.52477 -2.59757
H -0.70434 0.45961 -2.60677
H -0.81973 2.01294 -3.50461
H 0.65388 1.65766 -2.54072
Se 2.36679 1.45186 0.01454
C 3.00200 -0.35940 -0.28108
C 4.28301 -0.70036 0.17287
C 2.21951 -1.29744 -0.96959
C 4.78157 -1.98594 -0.06801
H 4.88833 0.02905 0.71722
C 2.71915 -2.58472 -1.18735
H 1.22384 -1.02794 -1.32922
C 4.00056 -2.93069 -0.74152
H 5.78204 -2.25038 0.28456

H 2.10424 -3.31799 -1.71578
H 4.38889 -3.93686 -0.91854
C 0.19193 0.30122 1.78650
C -0.05120 -1.16076 1.71756
H 0.95257 -1.61704 1.81806
H -0.46534 -1.47152 0.75067
H -0.67463 -1.51608 2.54979
C 0.50993 0.90882 3.10155
H 1.56630 0.64613 3.30079
H -0.10366 0.48161 3.90679
H 0.43545 2.00415 3.07707
O -1.45357 1.08514 1.19256
I -3.63816 -1.01379 -0.09784
H -2.20801 0.46679 0.85643

D

C -1.93730 -0.69355 0.34499
C -0.51296 -1.02868 0.18878
S 0.07624 -2.14575 -0.98632
C -1.46165 -2.79385 -1.71811
H -1.12703 -3.54062 -2.45256
H -2.08005 -3.27459 -0.94897
H -2.00945 -1.98829 -2.22629
Se -2.40406 0.72699 -0.90216
C -1.05671 2.01065 -0.35766
C 0.07364 2.20617 -1.16240
C -1.20960 2.72137 0.84126
C 1.05858 3.11449 -0.75974
H 0.19673 1.63667 -2.08628
C -0.21949 3.62521 1.23638
H -2.09114 2.56090 1.46626
C 0.91383 3.82157 0.43793
H 1.94756 3.25680 -1.37900
H -0.33280 4.17612 2.17377
H 1.68904 4.52432 0.75391
C -2.77996 -1.32400 1.19119
C -4.22486 -0.95557 1.35108
H -4.86056 -1.74329 0.90981
H -4.48108 -0.90759 2.42236
H -4.47900 0.00147 0.87628
C -2.32192 -2.49265 2.02256
H -2.96379 -3.36749 1.82208
H -1.27636 -2.78401 1.84826
H -2.43945 -2.25434 3.09336
O 0.30552 -0.39749 0.94172
I 3.45534 -0.60845 0.19296
H 1.31841 -0.52118 0.72370