SUPPORTING INFORMATION

Intramolecular Diels-Alder Reactions of Furan-tethered 1-Alkenesulfinic Acid Esters

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Synthetic Procedures and Spectroscopic Data

General procedure for 1-alkenesulfinyl chloride synthesis: To a solution of diphenylmethyl or p-methoxybenzyl 1-alkenyl sulfoxide in dry CH_2Cl_2 (1mmol/10mL) stirring at -78°C was added SO_2Cl_2 (1.2 eq., 1 M solution in CH_2Cl_2) via syringe. The mixture was stirred at -78°C for 10 min. and then warmed to rt until the fragmentation was complete (30 min.-1hr.).

Synthesis of 2-(2-furyl)ethyl ethenesulfinate (1a) using diphenylmethyl ethenyl sulfoxide. The reaction of diphenylmethyl ethenyl sulfoxide (2.90 g, 11.9 mmol) in CH_2Cl_2 (40 mL) with SO_2Cl_2 (13.2 mL, 13.2 mmol, 1M solution in SO_2Cl_2) and subsequent addition of 2-(2-furyl)ethanol (1.07 g, 9.58 mmol), and K_2CO_3 (8.28 g, 59.9 mmol) afforded sulfinate **1a** (1.17 g, 53%) as a colorless oil after flash chromatography on silica gel (10% EtOAc / hexanes). ^1H NMR (400 MHz), δ: 7.33 (d, *J* =1.9 Hz, 1H), 6.58 (dd, *J* =10.0 & 17.0 Hz, 2H), 6.30 (dd, *J* =1.9 & 3.4 Hz, 1H), 6.13 (d, *J* =17.0 Hz, 1H), 6.11 (d, *J* = 3.4 Hz, 1H), 5.99 (d, *J* = 10.0 Hz, 1H), 4.21 (t of ABq, *J* = 6.7 & 10.3 Hz, 2H), 3.03 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (100.6 MHz), δ: 151.12, 142.66, 141.55, 125.06, 110.32, 106.83, 63.57, 29.07; IR, cm^{-1}: 3121, 3042, 2956, 2931, 1616, 1506, 1379, 1129, 1012, 970; MS (CI, methane), m/z(%): 187(12), 105(13), 96(13), 95(100), 94(98), 81(82), 75(11), 67(11), 55(22), 53(23). Analysis calc'd for $C_8H_{10}O_3S$: C, 51.60; H, 5.41; found: C, 51.85; H, 5.60.

Cycloadditions of 2-(2-furyl)ethyl ethenesulfinate (1a).

Using $ZnBr_2$: A solution of 2-(2-furyl)ethyl ethenesulfinate (**1a**) (60.0 mg, 322 μmol) in dry toluene (3 mL) was added to a flask containing flame dried $ZnBr_2$ (2.0 eq) via a syringe. The mixture was stirred at rt for 5 d. After addition of ether (10 mL) and $NaHCO_3$ (aq) (10 mL), the layers were separated and the organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Filtration and concentration (aspirator) provided crude product. Flash chromatography on silica gel with 15% EtOAc / hexanes followed by 35% EtOAc / hexanes afforded cycloadduct **3a** (18 mg, 30%). Data for **3a**: ^1H NMR (400 MHz), δ: 6.53 (dd, *J* = 1.8 & 5.8 Hz, 1H), 6.08 (d, *J* = 5.8 Hz, 1H), 5.17 (dd, *J* = 1.8 & 4.7 Hz, 1H), 4.29 (m, 2H), 2.58 (ddd, *J* = 6.3, 11.9 & 15.3 Hz, 1H), 2.40 (dd, *J* = 3.1 & 8.0 Hz, 1H), 2.24 (m, 2H), 1.84 (dd, *J* = 8.0 & 12.6 Hz, 1H). ^{13}C NMR (100.6 MHz), δ: 139.15, 135.68, 87.71, 79.06, 63.84, 61.16, 29.01, 27.11; IR ($CDCl_3$), cm^{-1}: 3022, 2985, 1125, 1014, 825; MS (EI), m/z(%): 186(1), 151(3), 121(2), 120(4), 107(4), 95(21), 94(100), 92(2), 91(4), 90(1), 81(62), 79(3), 78(6), 77(5), 75(7), 67(6), 66(9), 65(7), 56(3), 55(25), 53(17), 52(3), 51(3). Analysis calc'd for $C_8H_{10}O_3S$: C, 51.60; H, 5.41; found: C, 51.64; H, 5.62.

__Using Et_2AlCl (rt)__: A solution of **1a** (60.0 mg, 322 μmol) in dry CH_2Cl_2 (2-3 mL) was added to a flask via a syringe and was taken to 0°C. To the flask was added Et_2AlCl (1.2 eq., 1.8 M solution) via syringe. After stirring for ten minutes, the mixture was warmed to rt and was stirred for 2 d. After addition of ether (10 mL) and $NaHCO_3$ (aq) (10 mL), the layers were filtered with suction through Celite, separated and the organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Filtration and concentration (aspirator) provided crude product. Chromatography as above afforded pure cycloadduct **3a** (26 mg, 43%).

__Using Et_2AlCl (62°C)__: A solution of **1a** (60.0 mg, 322 μmol) in dry toluene (2-3 mL) was added to a flask via a syringe and was taken to 0 °C. To the flask was added Et_2AlCl (1.2 eq, 1.8 M solution) via syringe. After stirring for ten minutes, the mixture was warmed to rt and heated at 62 °C for 7h.. Work-up as above provided crude product which was chromatographed as above to afford sulfinate **1a** (3 mg, 5%) followed by cycloadduct **3a** (29 mg, 53% based on recovered **1a**).

Using no catalyst: A solution of **1a** (60.0 mg, 322 μmol) in dry toluene (3 mL) was added to a flask containing BHT (0.1 eq, 7.10 mg, 32.2 μmol) and the solution was stirred until the BHT was dissolved. The mixture was heated at 68 °C for 24 d. Workup and chromatography as above for the Et_2AlCl reaction afforded **1a** (2 mg, 3%) and an inseparable isomeric mixture of cycloadducts **2a**/**3a** (31 mg, 54% based on recovered 1a) in a 1:1 ratio. Partial data for **2a**: ^1H NMR (400 MHz), δ: 6.56 (dd, *J* = 1.7 & 5.8 Hz, 1H), 6.03 (d, *J* = 5.8 Hz, 1H), 5.16 (d, *J* = 4.9 Hz, 1H), 4.74 (ddd, *J* = 2.0, 11.9 & 13.6 Hz, 1H), 3.81 (ddd, *J* = 1.6, 5.2 & 11.9 Hz, 1H), 2.64 (m, 1H), 2.39 (dd, *J* = 3.2 & 7.8 Hz, 1H), 2.33 (m, 2H), 1.65 (dd, *J* = 8.2 & 11.9 Hz, 1H). ^{13}C NMR (100.6 MHz), δ: 140.18, 136.65, 83.28, 78.46, 53.37, 51.75, 28.69, 27.37.

Oxidation of a mixture of cycloadducts 2a/3a. A solution of mCPBA (395 mg, 2.29 mmol) in SO_2Cl_2 (15 mL) was added dropwise to a 1:1 mixture of cycloadducts **2a**/**3a** (94.3 mg, 506 μmol) and BHT (33.5 mg, 152 μmol) in CH_2Cl_2 (15 mL) cooled to -78°C. After 10 minutes, the solution was warmed to rt and stirring continued for 5.5 hours. The solution was impinged with dry NH_3, and the resulting ppt. was removed by suction filtration through Celite. The filtrate was dried ($MgSO_4$), filtered and concentrated (aspirator) to afford crude product. Flash chromatography on silica gel with 45% EtOAc / hexanes afforded the corresponding sultone (82.9 mg, 81%) as a white crystalline solid, mp 129.5-131°C. ^1H NMR (400 MHz), δ: 6.60 (dd, *J* = 1.8 & 5.6 Hz, 1H), 6.09 (d, *J* = 5.6 Hz, 1H), 5.22 (dd, *J* = 1.8 & 4.7 Hz, 1H), 4.79 (ddd, *J* = 2.3, 11.7 & 13.4 Hz, 1H), 4.50 (ddd, *J* = 1.4, 5.6 & 11.7 Hz, 1H), 3.21 (dd, *J* = 3.5 & 8.0 Hz, 1H), 2.63 (ddd, *J* = 5.6, 13.4 & 15.6 Hz, 1H), 2.55 (ddd, *J* = 3.5, 4.7 & 12.3 Hz, 1H), 2.35 (d, *J* =

15.6 Hz, 1H), 1.85 (dd, *J* = 8.0 & 12.3 Hz, 1H). ^{13}C NMR (100.6 MHz), δ: 140.18, 135.45, 87.94, 78.72, 68.53, 57.88, 29.29, 27.25; IR ($CDCl_3$), cm^{-1}: 3018, 2972, 1605, 1360, 1175, 996, 800; MS (CI, methane), m/z(%): 202(1), 157(18), 141(25), 94(97), 93(17), 81(37), 78(15), 77(100), 66(10), 64(21). Analysis calc'd for $C_8H_{10}O_4S$: C, 47.52; H, 4.98; found: C, 47.71; H, 5.18.

Synthesis of 2-(2-furyl)ethyl (*E*)-carbomethoxyethenesulfinate (1b) using p-methoxybenzyl (*E*)-carbomethoxyethenyl sulfoxide. To the sulfinyl chloride from the reaction of p-methoxybenzyl (*E*)-carbomethoxyethenyl sulfoxide (114 mg, 0.452 mmol) in SO_2Cl_2 (10 mL) with SO_2Cl_2 (0.54 mL, 0.54 mmol), cooled to -78 °C was added K_2CO_3 (187 mg, 1.36 mmol) and BHT (10 mg, 0.045 mmol). After stirring for 10 min., 2-(2-furyl)ethanol (35.5 mg, 0.317 mmol) in CH_2Cl_2 (1 mL) was added and after 10 min., the solution was warmed to rt and stirred for ca. 19 hours. Filtration through Celite and concentration (aspirator) yielded the crude mixture which was quickly eluted through a silica gel plug (10-12 g) with hexanes / EtOAc. The fractions with product (<20% EtOAc) were concentrated and separated by flash chromatography on silica gel (10% EtOAc / hexanes) to afford sulfinate **1b** (70 mg, 64%) as a colorless oil that reacted rapidly. ^{1}H NMR (200 MHz), δ: 7.35 (d, *J* = 15.4 Hz, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 6.61 (d, *J* = 15.4 Hz, 1H), 6.31 (dd, *J* = 1.8 & 3.0 Hz, 1H), 6.12 (d, *J* = 3.0 Hz, 1H), 4.34 (m, 1H), 4.15 (m, 1H), 3.82 (s, 3H), 3.04 (t, *J* = 6.8 Hz, 2H).

Cycloadditions of 2-(2-furyl)ethyl (*E*)-2-carbomethoxyethenesulfinate (1b):

Using no catalyst, without prior purification of ***1b****:* After the fragmentation of p-methoxybenzyl (*E*)-2-carbomethoxyethenyl sulfoxide (145 mg, 0.610 mmol) with SO_2Cl_2 (0.73 mL, 0.73 mmol) the solution was cooled to -78°C. BHT (13.4 mg, 0.0610 mmol), K_2CO_3 (253 mg, 1.83 mmol) and 2-(2-furyl)ethanol (1 eq., 68.1 mg, 0.610 mmol) in CH_2Cl_2 (1 mL) were added. The mixture was warmed to -30 °C and stirred for 19 hr. Work-up as described above for **1b** (standard workup) and chromatography yielded **2b**/**3b** (inseparable 8.5:1 mixture of isomers, by ^{1}H NMR) as a white solid (66 mg, 47%). Recrystallization gave crystals of **2b** only, suitable for X-ray analysis. m.p. 102-103°C (EtOAc/hexanes).

2b: ^{1}H NMR (400 MHz), δ: 6.53 (dd, 1.7 & 5.6 Hz, 1H), 6.18 (d, *J* = 5.6 Hz, 1H), 5.31 (dd, *J* = 1.6 & 4.8 Hz, 1H), 4.39 (ddd, *J* = 2.0, 12.1 & 13.4 Hz, 1H), 3.82 (ddd, *J* = 1.7, 5.1 & 12.0 Hz, 1H), 3.71 (t(br), *J* = ca. 4.6 Hz, 1H), 3.69 (s, 3H), 3.01 (d, *J* = 4.1 Hz, 1H), 2.61 (ddd, *J* = 5.1, 13.4 & 15.2 Hz, 1H), 2.29 (dt, *J* = 1.7 & 15.2 Hz, 1H). ^{13}C NMR (100.6 MHz), δ: 170.63, 138.91, 138.26, 85.05, 79.46, 57.02, 52.41, 51.94, 47.84, 27.45.

3b: ^{1}H NMR (400 MHz), δ: 6.48 (dd, *J* = 1.7 & 5.6 Hz, 1H), 6.27 (d, *J* = 5.6, 1H), 5.31 (dd, *J* = 1.7 & 4.8 Hz, 1H), 4.39 (ddd, *J* = 2.2, 6.4 & 12.1 Hz, 1H), 4.36 (dt, *J* = 3.9 & 12.1 Hz, 1H), 3.69 (s, 3H), 3.49 (t(br), *J* = 3.9 Hz, 1H), 2.77 (d, *J* = 3.9 Hz, 1H), 2.68 (ddd, *J* = 6.4, 11.8 & 15.1 Hz, 1H), 2.28 (ddd, *J* = 2.2, 3.9 & 15.1 Hz, 1H).

Mixture of **2b**/**3b**: IR (neat) cm^{-1}: 2927, 1733, 1340, 1275, 1251, 1225, 1205, 1188, 1132, 1103, 879, 865, 838, 822, 732. MS (CI/methane) *m/z* (rel. intensity): 245(6, $[M+1]^+$), 213(17), 181(10), 179(21), 163(42), 149(28), 121(17), 119(9), 105(5), 96(6), 95(100), 94(6), 57(14). Anal. Calc'd for $C_{10}H_{12}O_5S$: C, 49.17; H, 4.95. Found: C, 49.23; H, 4.89.

*Using ZnBr$_2$, with prior purification of **1b***: To a flame-dried flask containing $ZnBr_2$ (1.2 eq., 19 mg, 0.35 mmol), a solution of **1b** (72 mg, 0.30 mmol) in CH_2Cl_2 (2 mL) was added at rt. The mixture was stirred for 3.5 hr and was quenched with $NaHCO_3$ (aq) (5 mL). The layers were separated and the aqueous layer was washed with CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated (aspirator). Purification by centrifugal chromatography yielded **2b**/**3b** (inseparable 4.3:1 mixture of isomers, by ^{1}H NMR) (56mg, 78%).

Cycloadditions of furfuryl (*E*)-2-carbomethoxyethenesulfinate (1d):

*At -30 °C, without prior purification of **1d**:* After fragmentation of p-methoxybenzyl (*E*)-2-carbomethoxyethenyl sulfoxide (257 mg, 1.01 mmol) with SO_2Cl_2 (1.10 mL, 1.11 mmol) the solution was cooled to -78°C. BHT (24 mg, 0.11 mmol), K_2CO_3 (456 mg, 3.30 mmol) and a solution of furfuryl alcohol (0.7 eq., 69 mg, 0.71 mmol) in dry CH_2Cl_2 (1 mL) were added. The mixture was warmed to -30 °C and stirred for 19 hrs. Standard work-up yielded **2d/3d** (inseparable 6:1 isomer ratio, by ^{1}H NMR) as a white solid (135 mg, 83%). Recrystallization gave crystals of **2d** only, suitable for X-ray analysis. m.p. 99°C (dec.) (EtOAc/hexanes).

2d: ^{1}H NMR (400 MHz), δ: 6.56 (m, 1H), 5.42 (dd, *J* = 4.6 & 1.3 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.74 (d, *J* = 11.0 Hz, 1H), 3.71 (s, 3H), 3.70 (m, 1H), 3.59 (d, *J* = 3.9 Hz, 1H). ^{13}C NMR (100.6 MHz), δ: 169.95, 137.79, 135.22, 98.30, 81.68, 75.44, 73.77, 52.48, 45.98.

3d: ^{1}H NMR (400 MHz), δ: 6.46 (ddd, *J* = 0.6, 1.5 & 5,8 Hz, 2H), 5.31 (dd, *J* = 4.6 & 1.5 Hz, 1H), 5.12 (d, *J* = 10.7 Hz, 1H), 4.73 (d, *J* = 10.7 Hz, 1H), 3.71 (s, 3H), 3.70 (m, 1H), 3.35 (d, *J* = 4.3 Hz, 1H).

Mixture of **2d**/**3d**: IR (neat) cm^{-1}: 2958, 1732, 1439, 1366, 1318, 1274, 1245, 1218, 1170, 1133, 1000, 918, 878. MS (EI) *m/z* (rel. intensity): 230(5, M^+), 166(39), 152(40), 134(46), 124(56), 121(40), 102(26), 97(21), 96(30), 95(35), 92(45), 82(51), 81(100), 79(45), 78(39), 77(37), 65(42), 59(59), 54(21), 53(59), 52(33), 51(39). Anal. Calc'd for $C_9H_{10}O_5S$: C, 46.94; H, 4.39%. Found: C, 46.79; H, 4.39%.

*<u>At -78 °C, without prior purification of **1d**</u>:* After fragmentation of <u>p</u>-methoxybenzyl (*E*)-2-carbomethoxyethenyl sulfoxide (257 mg, 1.01 mmol) with SO_2Cl_2 (1.10 mL, 1.11 mmol) the solution was cooled to -77°C. BHT (24 mg, 0.11 mmol), K_2CO_3 (456 mg, 3.30 mmol) and a solution of furfuryl alcohol (0.7 eq., 69 mg, 0.71 mmol) in dry CH_2Cl_2 (1 mL) were added and the mixture was stirred at -77 °C for 9 hrs. Standard work-up yielded **2d** as a lone product.

Cycloadditions of (*Z*)-2-carbomethoxyethyl PMB sulfoxide and furfuryl alcohol (1e): After fragmentation of <u>p</u>-methoxybenzyl (*Z*)-2-carbomethoxyethenyl sulfoxide (230 mg, 0.965 mmol) with SO_2Cl_2 (1.2 mL, 1.2 mmol) the solution was cooled to -78°C. Then K_2CO_3 (400 mg, 2.90 mmol) and furfuryl alcohol (1 eq., 95 mg, 0.97 mmol) in CH_2Cl_2 (1 mL) were added. The mixture was warmed to -50 °C and stirred for 19 hr. Standard work-up and chromatography yielded **2e** as a slightly brown solid as a single isomer (97 mg, 47%) m.p. 99°C (dec.) (EtOAc/hexanes). ^{1}H NMR (400 MHz), δ: 6.58 (dd, *J* = 1.7 & 5.7 Hz, 1H), 6.52 (d, *J* = 5.7 Hz, 1H), 5.39 (d, *J* = 1.7 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 3.79 (s, 3H), 3.27 (d, *J* = 8.8 Hz, 1H), 3.13 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100.6 MHz), δ: 170.08, 138.64, 131.54, 96.84, 83.94, 81.02, 71.49, 52.62, 47.53. IR cm^{-1}: 2955, 2360, 1744, 1224, 1179, 1120, 1092, 1060, 1029, 988, 942, 869. MS (EI) *m/z* (rel. intensity): 230 (7, M$^+$), 140(20), 124(59), 121(17), 96(23), 93(25), 82(23), 81(100), 79(41), 78(22), 77(19), 65(31), 59(40), 53(59), 51(19). Anal. Calc'd for $C_9H_{10}O_5S$: C, 46.94; H, 4.39. Found: C, 46.95; H, 4.38.

ORTEP Structure of Cycloadduct 2b

Summary of Crystal Data, Data Collection, Structure Solution and Refinement Details of Compound 2b

(a) **Crystal Data**

empirical formula	$C_{10}H_{12}O_5S$
molar mass	244.26
color, habit	colorless, block
crystal size, mm	.42 x .42 x .39
crystal system	orthorhombic
a, A	31.068(2)
b, A	4.8936(4)
c, A	6.8948(7)
α, °	90
β, °	90
γ, °	90
V, A^3	1048.24(16)
space group	$Pna2_1$
Z	4
F(000)	512
d_{calc}, g cm^{-3}	1.548
μ, mm^{-1}	0.312

(b) **Data acquisition**[a]

temp, K	294(1)
unit-cell reflcns (θ-range°)	9.5 22.0
max. θ (°) for reflcns	27.40
hkl range of reflcns	-40 40; -6 6; -8 8
variation in 3 standard reflcns	0.5%
reflcns measured	2383
unique reflcns	2383
reflcns with $I > 2\sigma(I)$,	2213
absorption correction type	psi-scans
min. max. abs. corr.	.8589, .9966

(c) **Structure Solution and Refinement**[b]

refinement on	F^2
solution method	direct methods
H-atom treatment	riding
no. of variables in L.S.	146
weights: either	
k in $w = 1/(\sigma^2 Fo^2 + k)$	$(0.0538P)^2+0.1349P$
$[P = (Fo^2 + 2Fc^2)/3]$	
R, R_w, *gof*	0.031, 0.081, 1.12
density range in final Δ-map, e A^{-3}	-0.214, 0.229
final shift/error ratio	0.002
sec. extnct. type	SHELXL
sec. extnct. correction	0.0025(17)

[a] Data collection on an Enraf Nonius CAD4 diffractometer with graphite monochromatised Mo-Kα radiation (λ 0.71067 A).

[b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E.J. Gabe, Y. Le Page, J-P. Charland, F.L. Lee and P.S. White, *J. Appl. Cryst.* (1989), **22**, 384-389) for refinement with observed data on F, or with SHELXL-93 for refinement with all data on F^2.

ORTEP Structure of Cycloadduct 2d

Summary of Crystal Data, Data Collection, Structure Solution and Refinement Details for Compound 2d

(a) **Crystal Data**

empirical formula	$C_9H_{10}O_5S$
molar mass	230.23
color, habit	colorless, lath
crystal size, mm	0.42 x 0.18 x 0.10
crystal system	monoclinic
a, A	7.3717(9)
b, A	15.698(2)
c, A	8.5766(9)
a, °	90
β, °	100.434(10)
γ, °	90
V, A^3	976.0(2)
space group	$P2_1/c$
Z	4
F(000)	480
d_{calc}, g cm^{-3}	1.567
μ, mm^{-1}	0.330

(b) **Data acquisition**[a]

temp, K	294(1)
unit-cell reflcns (θ-range°)	25 (10.3 18.2)
max. θ (°) for reflcns	27.41
hkl range of reflcns	-9 9; 0 20; 0 11
variation in 3 standard reflcns	1.0%
reflcns measured	2459
unique reflcns	2231
R_{int}	0.019
reflcns with $I > 2\sigma(I)$,	1401
absorption correction type	Gaussian integration
min. max. abs. corr.	0.9417, 0.9672

(c) **Structure Solution and Refinement**[b]

refinement on	F^2
solution method	direct methods
H-atom treatment	riding
no. of variables in L.S.	138
weights:	
k in $w = 1/(\sigma^2 Fo^2 + k)$	$(0.0551P)^2$
$[P = (Fo^2 + 2Fc^2)/3]$	
R, R_w, gof	0.044, 0.110, 1.00
density range in	
final Δ-map, e A^{-3}	-0.216, 0.372
final shift/error ratio	-0.001
sec. extnct. type	SHELXL
sec. extnct. correction	0.0032(18)

[a] Data collection on an Enraf Nonius CAD4 diffractometer with graphite monochromatised Mo-Kα radiation (λ 0.71067 A). [b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E.J. Gabe, Y. Le Page, J-P. Charland, F.L. Lee and P.S. White, *J. Appl. Cryst.* (1989), **22**, 384-389) for refinement with observed data on F, or with SHELXL-93 for refinement with all data on F^2.

Cartesian Coordinates for the Optimized Structures of Compounds 2f-5f, their Transition States for Formation and of two Conformations of Reactant 1f.

2f: (exo, pseudoaxial O)

Transition State

C	0.0013	-0.5435	-0.8945
C	1.4248	-0.5435	-0.8945
C	1.8050	0.7793	-0.8945
C	0.5925	1.5319	-0.8667
H	2.0495	-1.4191	-0.7743
H	2.8014	1.1849	-0.7786
H	0.4630	2.5708	-1.1446
O	-0.4222	0.6994	-1.2730
C	-1.0031	-1.6469	-1.0187
C	0.0058	1.3679	1.1132
C	-0.2331	-0.0109	1.2108
H	0.4727	-0.6664	1.7157
H	0.8497	1.7954	1.6466
H	-0.8605	2.0179	1.0177
S	-1.9044	-0.6781	1.2891
O	-1.5926	-1.9925	0.2589
H	-1.7899	-1.3420	-1.7156
H	-0.5392	-2.5708	-1.3725
O	-2.8014	0.3167	0.6325

Minimum

C	0.0713	-0.4704	-0.4028
C	1.5974	-0.4704	-0.4028
C	1.9411	0.8223	-0.4028
C	0.6240	1.5953	-0.4168
H	2.2278	-1.3452	-0.2929
H	2.9289	1.2572	-0.3063
H	0.6230	2.5922	-0.8574
O	-0.2258	0.7106	-1.1576
C	-0.7804	-1.6517	-0.8242
O	-1.8768	-1.7932	0.1080
S	-2.1680	-0.4668	1.1244
H	-1.1684	-1.4967	-1.8353
H	-0.2223	-2.5922	-0.7868
O	-2.9289	0.6184	0.4485
C	-0.3594	-0.0186	1.0407
C	-0.0321	1.4840	1.0085
H	-0.9496	2.0799	1.0213
H	0.6233	1.8023	1.8229
H	0.1277	-0.5901	1.8353

3f: (exo, pseudoequatorial O)

Transition State

C	-0.3032	-0.5514	-0.9625
C	1.1157	-0.5514	-0.9625
C	1.4929	0.7755	-0.9625
C	0.2836	1.5258	-0.9334
H	1.7437	-1.4228	-0.8310
H	2.4892	1.1797	-0.8408
H	0.1482	2.5655	-1.2045
O	-0.7341	0.6891	-1.3319
C	-1.3372	-1.6255	-1.0335
C	-0.3360	1.3410	1.0600
C	-0.5445	-0.0437	1.1546
H	0.1858	-0.6743	1.6556
H	0.5020	1.7789	1.5942
H	-1.1966	1.9993	0.9627
S	-2.1717	-0.8276	1.3401
O	-2.4891	-1.1873	-0.3001
H	-1.6967	-1.7928	-2.0539
H	-0.9400	-2.5655	-0.6331
O	-1.8453	-2.0990	2.0539

Minimum

C	-0.3104	-0.4849	-0.5804
C	1.2118	-0.4849	-0.5804
C	1.5541	0.8088	-0.5804
C	0.2391	1.5835	-0.5978
H	1.8461	-1.3563	-0.4687
H	2.5424	1.2429	-0.4836
H	0.2411	2.5791	-1.0415
O	-0.6136	0.6979	-1.3368
C	-1.1897	-1.6412	-0.9885
O	-2.5129	-1.2991	-0.5397
S	-2.5424	-0.5525	0.9900
H	-1.2471	-1.7588	-2.0730
H	-0.8499	-2.5791	-0.5311
O	-2.5388	-1.5780	2.0730
C	-0.7479	-0.0347	0.8559
C	-0.4236	1.4747	0.8226
H	-0.2687	-0.5921	1.6637
H	0.2294	1.7858	1.6420
H	-1.3287	2.0899	0.8467

4f: (exo, pseudoaxial O)

Transition State

C	-0.4516	-0.5818	-0.9015
C	0.9768	-0.5818	-0.9015
C	1.3521	0.7394	-0.9015
C	0.1417	1.4861	-0.8993
H	1.5977	-1.4517	-0.7492
H	2.3441	1.1503	-0.7664
H	0.0072	2.5346	-1.1345
S	-0.7394	-1.6834	1.6520
O	-0.8713	0.6638	-1.3347
O	-1.4541	-2.4372	0.2934
C	-1.3423	-1.7812	-1.0028
H	-2.3441	-1.4810	-1.3273
H	-0.9492	-2.5346	-1.6921
O	0.7328	-1.9194	1.6921
C	-0.2920	1.1419	1.1941
C	-1.0220	-0.0383	0.9857
H	0.6924	1.0872	1.6490
H	-0.8407	2.0592	1.3890
H	-2.0937	0.0735	0.8157

Minimum

C	-0.5709	-0.5509	-0.8281
C	0.9546	-0.5509	-0.8281
C	1.3108	0.7361	-0.8281
C	0.0038	1.4986	-0.7472
C	-0.5165	1.2764	0.7465
C	-1.1204	-0.1212	0.5726
H	1.5726	-1.4346	-0.7483
H	2.3014	1.1669	-0.7441
H	-0.0299	2.5249	-1.1112
H	0.3058	1.3246	1.4643
H	-1.2801	2.0058	1.0292
S	-0.8788	-1.6436	1.5638
H	-2.2099	-0.0530	0.4760
O	-0.8807	0.6572	-1.5341
O	-1.4090	-2.5249	0.1775
C	-1.2934	-1.8497	-1.1114
H	-2.3014	-1.6633	-1.4983
H	-0.7550	-2.5189	-1.7877
O	0.5832	-1.8234	1.7877

5f: (exo, pseudoequatorial O)

Transition State

C	-0.4360	-0.5504	-1.2526
C	0.9921	-0.5504	-1.2526
C	1.3658	0.7729	-1.2526
C	0.1566	1.5161	-1.2663
H	1.6122	-1.4252	-1.1127
H	2.3568	1.1889	-1.1245
H	0.0134	2.5648	-1.4923
S	-0.6848	-1.7032	1.3348
O	-0.8576	0.6879	-1.6864
O	-0.8829	-2.5648	-0.1723
C	-1.2889	-1.7872	-1.3064
H	-2.3568	-1.5368	-1.2886
H	-1.0888	-2.4197	-2.1779
O	-1.8777	-1.9911	2.1779
C	-0.2862	1.1295	0.8669
C	-0.9820	-0.0652	0.6266
H	0.7014	1.1176	1.3185
H	-0.8626	2.0302	1.0564
H	-2.0608	0.0283	0.4893

Minimum

C	-0.5582	-0.5103	-1.1007
C	0.9694	-0.5103	-1.1007
C	1.3241	0.7770	-1.1007
C	0.0118	1.5390	-1.0376
C	-0.5135	1.3342	0.4496
C	-1.0808	-0.0883	0.3017
H	1.5879	-1.3972	-1.0400
H	2.3138	1.2127	-1.0283
H	-0.0174	2.5601	-1.4158
H	0.2943	1.4384	1.1787
H	-1.3056	2.0426	0.7045
S	-0.7946	-1.5850	1.3340
H	-2.1753	-0.0530	0.2622
O	-0.8684	0.6882	-1.8183
O	-0.9006	-2.5601	-0.1165
C	-1.2298	-1.8463	-1.3327
H	-2.3138	-1.7458	-1.4661
H	-0.8102	-2.4335	-2.1538
O	-2.0226	-1.7664	2.1538

Two conformations of Reactant **1f**

Minimum

C	0.5382	-0.5837	-1.8371
C	1.9034	-0.5837	-1.8371
C	2.3184	0.7875	-1.8371
C	1.1742	1.5251	-1.8358
H	2.5383	-1.4591	-1.8366
H	3.3302	1.1678	-1.8410
H	0.9691	2.5849	-1.8415
O	0.0813	0.7109	-1.8400
O	-0.9344	-2.0151	-0.4974
C	-0.4745	-1.6703	-1.8341
H	-1.3405	-1.4131	-2.4532
S	-2.5180	-1.5727	-0.0769
H	-0.0243	-2.5849	-2.2281
O	-3.3302	-1.4655	-1.3279
C	-2.2052	0.1230	0.4344
C	-2.3976	0.4590	1.7084
H	-2.7052	-0.2724	2.4532
H	-2.2552	1.4788	2.0562
H	-1.9043	0.8095	-0.3527

Minimum

C	0.9650	-0.4769	-2.1962
C	2.3308	-0.4769	-2.1962
C	2.7428	0.8948	-2.1962
C	1.5961	1.6303	-2.1944
H	2.9671	-1.3513	-2.1955
H	3.7538	1.2773	-2.2014
H	1.3891	2.6897	-2.1980
O	0.5060	0.8156	-2.1973
O	-0.5175	-1.9094	-0.8405
C	-0.0552	-1.5583	-2.1715
H	-0.9144	-1.3005	-2.8012
S	-1.6830	-0.8343	-0.2122
H	0.3828	-2.4835	-2.5527
C	-1.6872	-1.7219	1.3575
C	-2.8353	-2.1849	1.8405
H	-3.7538	-2.0801	1.2682
H	-2.8848	-2.6897	2.8012
H	-0.7254	-1.7767	1.8591
O	-3.0078	-1.0762	-0.8553