Supporting Information

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Equilibrium and Kinetic Deuterium Isotopic Effects on the Hetero-Diels-Alder Addition of Sulfur Dioxide**

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General. Reagents and solvents are from Fluka, Buchs, Switzerland. Solvents are distilled before use. Anhydrous THF and Et₂O are distilled from Na/benzophenone, CH₂Cl₂ from CaH₂. Sulfur dioxide was dried by a column of basic alumina 90 (Merck, activity I). Kinetic measurements and NMR tube preparations for the reactions with sulfur dioxide, see [F. Monnat, P. Vogel, J. A. Sordo, Helv. Chim. Acta 2002, 85, 712]. Spectral recording, see [K. Kraehenbuehl, S. Picasso, P. Vogel, Helv. Chim. Acta 1998, 81, 1439].

cis-(3,3⁻²H₂)-3a,4,5,6,7,7a-Hexahydro-2-benzofuran-1(3H)-one (8). A suspension of NaBD₄ (5 g, 0.119 mol, 98 atom % D, Fluka) in anhydrous tetrahydrofuran (THF, 23 mL), was added dropwise to a stirred solution of cis-cyclohexane-1,2-dicarboxylic anhydride (18.4 g, 0.119 mol) in anhydrous THF (120 mL) cooled to 0 °C and under Ar atmosphere. The white suspension is then stirred at 20 °C for 2 days and 5 M aqueous HCl (50 mL) was added slowly at 0 °C. Water (60 mL) was added and the mixture extracted with Et₂O (90 mL, 4 times). The combined ethereal extracts were washed with H₂O (100 mL, twice), dried (MgSO₄) and the solvent was evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (light petroleum ether/AcOEt
2:1), giving a colorless oil (13.8 g, 81%), b.p. 100 °C (1 Torr). UV \((\text{CH}_3\text{CN}) \lambda_{\text{max}}: 212 (\varepsilon = 300)\). IR (film) \(\nu: 2935, 2885, 2855, 1780, 1450, 1360, 1330, 1210, 1120, 1045, 990, 980, 915, 855 \text{ cm}^{-1}\). \(^1\text{H-NMR} \text{(400 MHz, CDCl}_3\) \(\delta_H: 2.66-2.62 \ (m, \text{H-C(7a)}), 2.48-2.43 \ (m, \text{H-C(3a)}), 2.14-2.09 \ (m, \text{H}_a\text{-C(7)}), 1.85-1.79 \ (m, \text{H}_a\text{-C(4)}), 1.67-1.57 \ (m, \text{H}_b\text{-C(7)}, \text{H}_a\text{-C(6), et H}_a\text{-C(5)}), 1.27-1.18 \ (m, \text{H}_b\text{-C(4), H}_b\text{-C(6), H}_b\text{-C(5)}). \) Signals at \(\delta_H 4.2 \& 3.92 \text{ ppm show less than 2\% of H.} \) \(^{13}\text{C-RMN} \text{(100.6 MHz, CDCl}_3\) \(\delta_C: 178.5 \ (s, \text{C}(1)), 71.1 \ (\text{quint, } ^1\text{J(C,D)}=22, \text{C}(3)),\) 39.4 \ (d, ^1\text{J(C,H)}=126, \text{C(7a)}), 35.2 \ (d, ^1\text{J(C,H)}=135, \text{C(3a)}), 27.1 \ (t, ^1\text{J(C,H)}=128, \text{C(4)}), 23.4 \ (t, ^1\text{J(C,H)}=128, \text{C(5)}), 22.9 \ (t, ^1\text{J(C,H)}=128, \text{C(7)}), 22.5 \ (t, ^1\text{J(C,H)}=128, \text{C(6)}). \) \(^2\text{H-NMR} \text{(61.4 MHz, CDCl}_3\) \(\delta_D: 4.20 \ (s, \text{D}_a\text{-C(3)}), 3.95 \ (s, \text{D}_b\text{-C(3)}). \) CI-MS (NH\(_3\)) \(m/z: 143 ([\text{M+H}^+], \ 7), 142 (\text{M}^+, \ 7), 97 ([\text{M+H}^+-\text{CO}_2], \ 27), 83 (85), 81 (100). \) Anal. calcd. for C\(_8\)H\(_{10}\)D\(_2\)O\(_2\) (142.19): H 7.09, C 67.58; found: H 7.20, C 67.70.

cis-Cyclohexane-1,2-(\(\alpha,\alpha^2\text{H}_2\))-dimethanol (9). Lactone 8 (3 g, 21.1 mmol) was added portionwise to a stirred suspension of LiAlH\(_4\) (1.6 g, 42.2 mmol) in anhydrous THF (44 mL) under Ar atmosphere. The mixture was stirred at 20 °C for 1 h and a saturated aqueous solution of NH\(_4\)Cl (12 mL) was added
portionwise. 

Et₂O (30 mL), then H₂O (10 mL) were added. The precipitate was taken off by filtration on Celite, rinsing with Et₂O. The solvent was evaporated *in vacuo* yielding a white solid (2.92 g, 95%), m.p. 39–40 °C. UV (CH₃CN) \( \lambda_{\text{max}} : 192 \) (\( \varepsilon = 200 \)). IR (KBr) \( \nu : 3340, 2925, 2860, 1450, 1355, 1145, 1095, 1075, 1040, 1025, 970, 675 \) cm\(^{-1}\). ¹H-NMR (400 MHz, CDCl₃) \( \delta_H : 3.79 \) (\( dd, \ 2J(H_a-C(α'), H_b-C(α'))=11.0, \ 3J(H_a-C(α'), H-C(2))=8.0, \ H_a-C(α') \)), 3.60 (\( dd, \ 2J(H_a-C(α'), H_b-C(α'))=11.0, \ 3J(H_a-C(α'), H-C(2))=4.0, \ H_b-C(α') \)), 2.29 (\( s, \ H-OC(α), H-O C(α') \)), 1.95 (\( m, \ H-C(1), H-C(2) \)), 1.56–1.37 (\( m, \ H_2-C(3), H_2-C(4), H_2-C(5), H_2-C(6) \)). ¹³C-NMR (100.6 MHz, CDCl₃) \( \delta_C : 63.8 \) (\( t, \ 1J(C,H)=140, C(α') \)), 63.0 (\( quint, \ 1J(C,D)=21, C(α) \)), 39.7 (\( d, \ 1J(C,H)=129, C(2) \)), 39.6 (\( d, \ 1J(C,H)=129, C(1) \)), 27.0 (\( d, \ 1J(C,H)=125, C(3), C(6) \)), 23.9 (\( t, \ 1J(C,H)=127, C(4), C(5) \)). ²H-NMR (61.4 MHz, CDCl₃) \( \delta_D : 3.75 \) (\( s, \ D_a-C(α') \)), 3.575 (\( s, \ D_b-C(α') \)). CI-MS (NH₃) \( m/z : 147 \) ([M+H⁺], 0.3), 128 ([M−H−OH]⁺, 3), 111 ([M+H⁺−2×H−2×OH], 23), 98 (83), 96 (86), 81 (100).

Anal. calcd. for C₈H₁₄D₂O₂ (146.22): H 9.65, C 65.71; found: H 9.41, C 65.77.
cis-Cyclohexane-1,2-(α,α-²H₂)-dimethyl bis(paratoluene-sulfonate) (10). A solution of diol 9 (5.97 g, 40.8 mmol) in anhydrous pyridine (26 mL) was added dropwise to a stirred mixture of paratoluenesulfonyl chloride (24.4 g, 120 mmol), 4-dimethylaminopyridine (0.781 g, 6.4 mmol) in anhydrous pyridine (20 mL) cooled to 0 °C and under Ar atmosphere. After stirring at 20 °C for 25 min, H₂O (40 mL) was added and the mixture stirred at 20 °C for 20 min. The precipitate was collected (Büchner filter), washed with H₂O, then with MeOH. It was then dried in vacuo, yielding a white solid (12.9 g, 69%), m.p. 79-80 °C. UV (CH₃CN) λ<sub>max</sub>: 272 (ε = 2100), 261 (2500), 224 (22'900), 200 (15'900). IR (KBr) ν: 3035, 2930, 2860, 1600, 1350, 1190, 1175, 960, 940, 820, 665, 555 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) δ<sub>H</sub>: 7.77 (d, ³J(H-C(3'), H-C(2'))=8.0, 4xH-C(2')), 7.37 (d, ³J(H-C(3'), H-C(2'))=8.0, 4xH-C(3')), 3.91 (d, ³J(H-C(1), H-C(α'))=7.0, H₂-C(α')), 2.47 (s, 2xMe), 2.04 (m, H-C(1), H-C(2)), 1.40-1.30 (m, H₂-C(3), H₂-C(4), H₂-C(5) et H₂-C(6)). ¹³C-NMR (100.6 MHz, CDCl₃) δ<sub>C</sub>: 144.9 (s, 2C(4')), 132.7 (s, 2C(1')), 129.9 (d, ¹J(C,H)=161, 4C(3')), 127.8 (d, ¹J(C,H)=166, 4C(2')), 70.3 (t, ¹J(C,H)=148, C(α')), 69.6 (quint, ¹J(C,D)=22, C(α)), 36.4 (d, ¹J(C,H)=130, C(2)), 36.2 (d, ¹J(C,H)=130, C(1)), 25.7 (t,
$^1J(C,H) = 128, \ C(3), \ 25.6 \ (t, \ ^1J(C,H) = 128, \ C(6), \ 22.8 \ (t,$

$^1J(C,H) = 129, \ C(4), \ 22.7 \ (t, \ ^1J(C,H) = 129, \ C(5)), \ 21.6 \ (q,$

$^1J(C,H) = 127, \ 2\times \text{Me}). \ ^2\text{H-NMR (61.4 MHz, CDCl}_3) \delta_D: 3.90 \ (s, \ D_2-\text{C(}\alpha))$. \ CI-MS (NH$_3$) $m/z$: 472 ([M+NH$_4^+$], 100), 471 ([M+NH$_3^+$], 69), 454 ([M]$^+$, 0.6), 283([M-OTs]$^+$, 19), 155 (Ts$^+$, 8), 112 ([M-2×OTs]$^+$, 6), 111 (56), 110 (32). \ Anal. \ calcd. \ for \ C$_{22}$H$_{26}$D$_2$O$_6$S$_2$ (454.59): H 5.76, C 58.13; found: H 5.73, C 58.06.

1-[(^2H$_2$)-Methylidene]-2-methylidenecyclohexane (3). \ Bistosylate 10 (7.2 g, 15.8 mmol) was added portionwise to a stirred solution of t-BuOK (7.1 g) in anhydrous DMSO (63 mL). After stirring at 25 °C for 35 min, the mixture was cooled to 0 °C and H$_2$O (60 mL) was added. The mixture was extracted with pentane (50 mL, 3 times). The combined extracts were washed with saturated aqueous solution of NH$_4$Cl (20 mL, twice) and dried (MgSO$_4$). Solvent distillation at 1 atmosphere, then distillation of the residue under reduced pressure, b.p. 30 °C (600 mbar). The crude diene 3 is then redistilled with a Vigreux column, b.p. 46-50 °C (80 mbar), colorless liquide (900 mg, 52%). \ UV (CH$_3$CN) $\lambda_{max}$: 221 ($\epsilon = 4000$). \ IR (film) $\nu$: 3080, 2935, 2885, 2860, 2840, 1630, 1595, 1440, 1260, 1100, 1020, 890, 820, 805, 740, 715 cm$^{-1}$. \ $^1\text{H-NMR}$
(400 MHz, CD$_2$Cl$_2$) $\delta_H$: 4.94 (dm, $^2J(H_{\text{cis}}-C(2'), H_{\text{trans}}C(2'))=2.6,$ $H_{\text{cis}}-C(2'))$, 4.67 (dm, $^2J(H_{\text{cis}}-C(2'), H_{\text{trans}}C(2'))=2.6,$ $H_{\text{trans}}-C(2'))$, 2.30–2.27 (m, $H_2$-C(3), $H_2$-C(6)), 1.68–1.65 (m, $H_2$-$C(4)$, $H_2$-C(5)). $^{13}$C-NMR (100.6 MHz, CD$_2$Cl$_2$) $\delta_C$: 150.2 (s, C(2)), 150.1 (s, C(1)), 107.9 (t, $^1J(C,H)=156$, C(2')), 107.4 (quint, $^1J(C,D)=24$, C(1')), 35.7 (t, $^1J(C,H)=126$, C(3)), 35.6 (t, $^1J(C,H)=126$, C(6)), 27.2 (2× t quint, $^1J(C,H)=128$, $^2J(C,H)=5$, C(4), C(5)). $^2$H-NMR (61.4 MHz, CDCl$_3$) $\delta_D$: 4.97 (s, $D_{\text{cis}}-C(1'))$, 4.70 (s, $D_{\text{trans}}-C(1')$). GC-CI-MS (NH$_3$) m/z: 128 ([M+NH$_4^+$], 10), 111 ([M+H$^+$], 100), 110 (M$^+$, 32), 95 (6), 79 (2).

(4,4-$^2$H$_2$)-1,4,5,6,7,8-Hexahydro-2,3-benzoxathiine-3-oxide (4), (1,1-$^2$H$_2$)-1,4,5,6,7,8-hexahydro-2,3-benzoxathiine-3-oxide (5) and (1,1-$^2$H$_2$)-1,3,4,5,6,7-hexahydrobenzo[c]thiophene 2,2-dioxide (6). A mixture of diene 3 (11.6 mg, 0.21 molar), anhydrous sulfur dioxide (233 mg, 7.31 molar) in CDCl$_2$ (total volume of 0.5 mL) was made in a 5 mm pyrex NMR tube (vac. line, bulb-to-bulb distillation, liquid N$_2$). The NMR tube was left at -75 °C. After 780 min ($^1$H-NMR) 99% conversion was reached and a 51.4/46.5/2.1 mixture of 4, 5 and 6 was formed.
Sultines 4 and 5 are equilibrated first and then converted into 6 in a few minutes at -40 °C.

Data for 4: $^1$H-NMR (400 MHz, CD$_2$Cl$_2$/CFCl$_3$/SO$_2$, 213K) $\delta_H$: 4.27 (d, $^3J$(H$_a$-C(1), H$_b$-C(1))=15.8, H$_a$-C(1)), 4.12 (d, $^3J$(H$_a$-C(1), H$_b$-C(1))=15.8, H$_b$-C(1)), 1.91-1.89 (m, H$_2$-C(5)), 1.85-1.83 (m, H$_2$-C(8)), 1.78-1.72 (m, H$_a$-C(6), H$_a$-C(7)), 1.58-1.50 (m, H$_b$-C(6), H$_b$-C(7)). $^{13}$C-NMR (100.61 MHz, CD$_2$Cl$_2$/CFCl$_3$/SO$_2$, 213K) $\delta_C$: 125.8 (s, C(8a)), 117.4 (s, C(4a)), 60.0 (t, $^1J$(C,H)=150, C(1)), 49.0 (quint, $^1J$(C,D)=20, C(4)), 29.0 (t, $^1J$(C,H)=127, C(5)), 24.8 (t, $^1J$(C,H)=127, C(8)), 22.1 (t, $^1J$(C,H)=129, C(6)), 21.4 (t, $^1J$(C,H)=127, C(7)). $^2$H-NMR (61.4 MHz, CD$_2$Cl$_2$/CFCl$_3$/SO$_2$, 203K) $\delta_D$: 3.38 (br. s, D$_a$-C(4)), 2.72 (br. s, D$_b$-C(4)). $^{17}$O-NMR (54.2 MHz, CD$_2$Cl$_2$/CFCl$_3$/SO$_2$, 213K) $\delta_{17O}$: 133 (br. s, $\nu_\beta$=1080, O=S(3)), 77 (br. s, $\nu_\beta$=1790, O(2)).

Data for 5: $^1$H-NMR (400 MHz, CD$_2$Cl$_2$/CFCl$_3$/SO$_2$, 213K) $\delta_H$: 3.40 (dm, $^3J$(H$_a$-C(4), H$_b$-C(4))=17.0, H$_a$-C(4)), 2.73 (dm, $^3J$(H$_a$-C(4), H$_b$-C(4))=17.0, H$_b$-C(4)), 1.91-1.89 (m, H$_2$-C(5)), 1.85-1.83 (m, H$_2$-C(8)), 1.78-1.72 (m, H$_a$-C(6), H$_a$-C(7)), 1.58-1.50 (m, H$_b$-C(6), H$_b$-C(7)). $^{13}$C-NMR (100.61 MHz, CD$_2$Cl$_2$/CFCl$_3$/SO$_2$, 213K) $\delta_C$: 125.6 (s, C(8a)), 117.6 (s, C(4a)), 59.3 (quint, $^1J$(C,D)=22, C(1)), 49.6 (t, $^1J$(C,H)=137, C(4)), 29.1 (t,
$^1J(C,H)$=127, C(5)), 24.8 (t, $^1J(C,H)$=127, C(8)), 22.1 (t, $^1J(C,H)$=129, C(6)), 21.4 (t, $^1J(C,H)$=127, C(7)). $^2$H-NMR (61.4 MHz, CD$_2$Cl$_2$/CFC$_3$/SO$_2$, 203K) $\delta_d$: 4.24 (br. s, D$_a$–C(1)), 4.11 (br. s, D$_b$–C(1)). $^{17}$O-NMR (54.2 MHz, CD$_2$Cl$_2$/CFC$_3$/SO$_2$, 213K) $\delta_{^{17}O}$: 133 (br. s, $\nu_a$=1080, O=S(3)), 77 (br. s, $\nu_a$=1790, O(2)).

Example of kinetic measurements 3 + (SO$_2$)$_2$ ⇄ 4 + 5 + SO$_2$ ⇄ 6

Simulation of the kinetics $3 + (\text{SO}_2)_2 \rightleftharpoons 4 + 5 + \text{SO}_2 \rightleftharpoons 6 + \text{SO}_2$

$^{13}$C-NMR spectrum of $1 + 3 + \text{SO}_2 \rightleftharpoons 4 + 5 + 2$. 
\[
\begin{align*}
\text{3} & \quad \text{D} \quad \text{D} \\
\text{1} & \quad \text{SO}_2 \\
\text{S} & \quad \text{O} \\
\text{O} & \quad \text{D} \\
\text{S} & \quad \text{O} \\
\text{D} & \quad \text{S} \\
\end{align*}
\]

\(-75^\circ\text{C}\)

\[
\begin{align*}
\text{4} & \quad \text{D} \quad \text{D} \quad \text{S} \\
\text{5} & \quad \text{D} \quad \text{D} \quad \text{S} \\
\text{2} & \quad \text{D} \quad \text{D} \quad \text{S} \\
\end{align*}
\]

**Peak 1/T2**

1: 1.5833e+001 ± 1.17e+000
2: 2.0207e+001 ± 4.54e-001

**Peak height**

1: 7.9564e+003 ± 4.03e+002
2: 2.3289e+004 ± 3.57e+002

**Rel. integrals (%)**

1: 21.11± 3.82
2: 78.89± 7.42

**NMR Spectra**

- Dienes (1+3)
- Toluene
- Dienes (1+3)
- Sultines
Kinetics of the disappearance of dienes $1 + 3$ at $-75 \, ^\circ \text{C}$, 
$[\text{SO}_2]_o = 2.76 \, \text{moldm}^{-3}$, $[1]_o = 0.21 \, \text{moldm}^{-3}$, $[3]_o = 0.11 \, \text{moldm}^{-3}$