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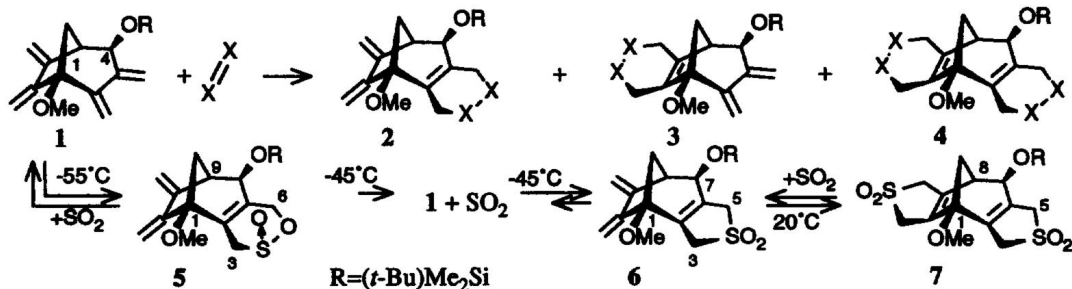
# Site- and Regioselectivity of the Hetero-Diels-Alder and Cheletropic Additions of Sulfur Dioxide to a 2,3,6,7-Tetramethyldienebicyclo[3.2.1]octane Derivative.

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**Summary:** At  $-55^{\circ}\text{C}$   $\text{SO}_2$  adds to 4-[(*tert*-butyl)dimethylsilyloxy]-1-methoxy-2,3,6,7-tetramethyldienebicyclo[3.2.1]octane reversibly and selectively onto the *s*-cis-butadiene moiety at C(2), C(3) giving a single regioisomeric sultine. At  $-45^{\circ}\text{C}$  the cheletropic addition of  $\text{SO}_2$  occurs selectively giving the monosulfolene attached at C(2), C(3).

Simple 1,3-dienes such as isoprene and (E)-piperilene undergo hetero-Diels-Alder additions below  $-60^{\circ}\text{C}$  and give the corresponding 3,6-dihydro-1,3-oxathiin-2-oxides (sultines) with high regioselectivity.<sup>1</sup> The sultines are unstable above  $-50^{\circ}\text{C}$  and undergo cycloreversion liberating the starting dienes and  $\text{SO}_2$  that undergo cheletropic additions<sup>2</sup> above  $-40^{\circ}\text{C}$  giving the corresponding sulfolenes.<sup>3</sup> The Diels-Alder additions of the exocyclic tetraene **1** to strong dienophiles ( $\text{X}=\text{X}$ ) such as ethylenetetracarbonitrile, dimethyl acetylenedicarboxylate and maleic anhydride were not site selective and gave mixture of the corresponding monoadducts **2** and **3** together with the bis-adducts **4**.<sup>4</sup> No significant regioselectivity was noticed for the cycloaddition of **1** to methyl propionate and methyl vinyl ketone. In contrast with these results, we report here that  $\text{SO}_2$  adds to tetraene **1** with high site-selectivity for both its hetero-Diels-Alder and cheletropic additions, the *s*-cis-butadiene moiety at C(2), C(3) being preferred over that at C(6), C(7). Furthermore, in the case of the hetero-Diels-Alder addition **1** +  $\text{SO}_2$  only one single regioisomeric sultine was observed.

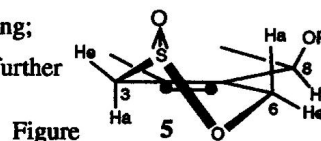


When a 0.2 M solution of **1** in  $\text{CD}_2\text{Cl}_2/\text{SO}_2$  7:1 (w/w) was allowed to stand at  $-55^{\circ}\text{C}$  (5 mm sealed NMR tube) the monosultine **5** was formed slowly. After 2 days at  $-55^{\circ}\text{C}$ , 50% of **5** was formed together with <5% of sulfolene **6** and ca. 5% of an unknown compound the  $^1\text{H}$ -NMR spectrum of which was not consistent with an isomeric sultine or sulfolene. After 7 days at  $-55^{\circ}\text{C}$ , nearly 95% of **1** had reacted. At  $-45^{\circ}\text{C}$ , sultine **5** underwent cycloreversion into **1** +  $\text{SO}_2$  that reacted slowly to give **6** which was obtained in 85% yield after 24 h at  $0^{\circ}\text{C}$ . The cheletropic addition of a second equivalent of  $\text{SO}_2$  to give the bis-sulfolene **7** was a very slow process at  $0^{\circ}\text{C}$ . A good yield of **7** (70-80%) was obtained when **6** was reacted with a large excess  $\text{CD}_2\text{Cl}_2/\text{SO}_2$  1:5 (w/w) at  $20^{\circ}\text{C}$  for 24 h. After prolonged standing at  $0$ - $20^{\circ}\text{C}$ , **6** did not equilibrate with an isomeric sulfolene. One cannot exclude yet that both **5** and **6** are preferred for thermodynamic reasons rather than for kinetic reasons. Because **7** decomposed on heating, we could not establish whether **6**

was formed or not by elimination of SO<sub>2</sub>.

The structures of **5**,<sup>5</sup> **6**<sup>6</sup> and **7**<sup>7</sup> were deduced from their <sup>1</sup>H- and <sup>13</sup>C-NMR spectra and with the help of double irradiation experiments. In the case of **5** the homoallylic coupling constants <sup>5</sup>J<sub>H,H</sub> between protons H-C(3) on one hand, and protons H-C(6) and H-C(8), on the other hand,<sup>8</sup> allowed one to distinguish between pseudo-equatorial and pseudo-axial protons at C(3) and C(6). Strong NOE's were observed between the proton pairs H-C(8)/H-C(9), H-C(8)/H<sub>e</sub>-C(6) consistently with the conformation shown for **5** in the Fig. NOE was also observed between the olefinic protons and H-C(9) and MeO protons. The axial S O moiety of **5** was assumed.<sup>9</sup>

The selectivities reported here for the reaction of **1** with SO<sub>2</sub> are striking; they rise a number of questions to which we hope to propose answers when further reactions of SO<sub>2</sub> with polyenes analogous to **1** will have been examined.



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#### References and Notes

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5. Data of **5**: <sup>1</sup>H-NMR (Bruker, ARX 400, CD<sub>2</sub>Cl<sub>2</sub>/SO<sub>2</sub>, -55°C) δ<sub>H</sub>: 5.5, 5.2, 5.1, 4.8 (4s, H<sub>2</sub>C=C(10), H<sub>2</sub>C=C(11)), 4.57 (ddd, <sup>2</sup>J=15, <sup>5</sup>J(H<sub>a</sub>-C(6),H<sub>a</sub>-C(3))=3, <sup>5</sup>J(H<sub>a</sub>-C(6),H<sub>e</sub>-C(3))=2, H<sub>a</sub>-C(6)), 4.20 (dd, <sup>2</sup>J=15, <sup>5</sup>J(H<sub>a</sub>-C(6),H<sub>a</sub>-C(3))=1.0, H<sub>e</sub>-C(6)), 3.82 (dd, <sup>3</sup>J=2, <sup>5</sup>J(H<sub>a</sub>-C(3),H-C(8))=1.0, H-C(8)), 3.53 (dddd, <sup>2</sup>J=17, <sup>5</sup>J(H<sub>a</sub>-C(3),H<sub>a</sub>-C(6))=3, <sup>5</sup>J(H<sub>a</sub>-C(3),H<sub>e</sub>-C(6)) = <sup>5</sup>J(H<sub>a</sub>-C(3),H-C(8))=1.0, H<sub>a</sub>-C(3)), 3.06 (dd, <sup>2</sup>J=17, <sup>5</sup>J(H<sub>a</sub>-C(6),H<sub>e</sub>-C(3))=2, H<sub>e</sub>-C(3)), 2.85 (dd, <sup>3</sup>J=6, 2, H-C(9)), 2.28 (d, <sup>2</sup>J=10, H<sub>syn</sub>-C(12)), 1.92 (dd, <sup>2</sup>J=10, <sup>3</sup>J=6, H<sub>anti</sub>-C(12)), 0.90 (s, t-Bu), 0.16 & 0.15 (2s, Me<sub>2</sub>Si); <sup>13</sup>C-NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -55°C) δ<sub>C</sub>: 148.0, 145.0 (2s, C(10), C(11)), 129.4, 127.4 (2s, C(2), C(7)), 109.2, 101.0 (2t, <sup>1</sup>J=160, C(10), C(11)), 83.6 (s, C(11)), 73.3 (d, <sup>1</sup>J=145, C(8)), 59.7 (t, <sup>1</sup>J=151, C(3)), 52.1 (q, <sup>1</sup>J=142, MeO), 46.3 (d, <sup>1</sup>J=140, C(9)), 44.8 (t, <sup>1</sup>J=140, C(6)), 31.3 (t, <sup>1</sup>J=135, C(12)), 25.3 (q, <sup>1</sup>J=125, t-Bu), 17.7 (s, SiC), -5.1, -5.2 (2q, <sup>1</sup>J=118, Me<sub>2</sub>Si).
6. Data of **6**: <sup>1</sup>H-NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>/SO<sub>2</sub>, 0°C) δ<sub>H</sub>: 5.62, 5.38, 5.22, 4.95 (4s), 4.0-3.9 (m, H<sub>a</sub>-C(3), H<sub>a</sub>-C(5), H-C(7)), 3.8-3.72 & 3.62-3.60 (2m, H<sub>b</sub>-C(3), H<sub>b</sub>-C(5)), 3.33 (s, MeO), 2.98 (m, H-C(8)), 2.22 (d, <sup>2</sup>J=10) & 1.93 (dd, <sup>2</sup>J=10, <sup>3</sup>J=6, H<sub>2</sub>C(11)), 0.95 (s, t-Bu), 0.20 & 0.15 (2 s, Me<sub>2</sub>Si); <sup>13</sup>C-NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>/SO<sub>2</sub>, 0°C) δ<sub>C</sub>: 147.4, 145.3, 139.9, 128.6 (4s), 109.7 (t, 2C, <sup>1</sup>J=159), 84.3 (s, C(1)), 72.4 (d, <sup>1</sup>J=146, C(7)), 58.8 (t, <sup>1</sup>J=143, C(3)), 55.7 (t, <sup>1</sup>J=157, C(5)), 52.6 (q, <sup>1</sup>J=143, MeO), 47.4 (d, <sup>1</sup>J=141, C(8)), 31.8 (t, <sup>1</sup>J=135, C(11)), 25.8 (q, <sup>1</sup>J=125), 18.3 (s), -4.61 & -4.74 (2 q, <sup>1</sup>J=119).
7. Data of **7**: <sup>1</sup>H-NMR (360 MHz, SO<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub>, 20°C) δ<sub>H</sub>: 4.1 (m, H-C(7)), 4.0-3.75 (m, 8H, H<sub>2</sub>C(3), H<sub>2</sub>C(5), H<sub>2</sub>C(10), H<sub>2</sub>C(12)), 3.35 (s, MeO), 3.08 (m, H-C(8)), 2.58 (dd, <sup>2</sup>J=10, <sup>3</sup>J=5) & 2.45 (d, <sup>2</sup>J=10, H<sub>2</sub>C(14)), 0.90 (s, t-Bu), 0.16, 0.15 (2s, Me<sub>2</sub>Si); <sup>13</sup>C-NMR (100.6 MHz, SO<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub>, 20°C) δ<sub>C</sub>: 125.5 (s, C(2), C(4)), 115.6, 113.9 (2s, C(6), C(9)), 70.9 (s, C(1)), 65.3 (d, <sup>1</sup>J=143, C(7)), 58.3, 57.0, 56.8, 56.1 (4t, <sup>1</sup>J=146), 52.9 (q, <sup>1</sup>J=143, MeO), 47.2 (d, <sup>1</sup>J=144, C(8)), 40.8 (t, <sup>1</sup>J=138, C(14)), 26.1 (q, <sup>1</sup>J=125), 18.7 (s), -4.5, -4.6 (2q).
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