

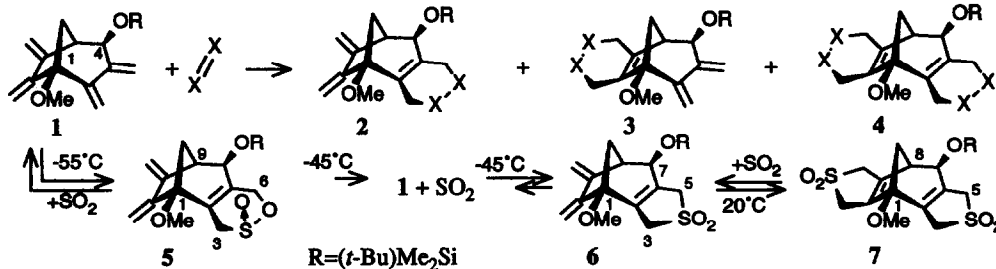
Site- and Regioselectivity of the Hetero-Diels-Alder and Cheletropic Additions of Sulfur Dioxide to a 2,3,6,7-Tetramethylidenebicyclo[3.2.1]octane Derivative.

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Summary: At -55°C SO_2 adds to 4-[(*tert*-butyl)dimethylsilyloxy]-1-methoxy-2,3,6,7-tetramethylidenebicyclo[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°C the cheletropic addition of 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°C and give the corresponding 3,6-dihydro-1,3-oxathiin-2-oxides (sultines) with high regioselectivity.¹ The sultines are unstable above -50°C and undergo cycloreversion liberating the starting dienes and SO_2 that undergo cheletropic additions² above -40°C giving the corresponding sulfolenes.³ 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**.⁴ 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 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** + SO_2 only one single regioisomeric sultine was observed.

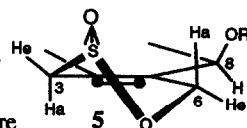


When a 0.2 M solution of **1** in $\text{CD}_2\text{Cl}_2/\text{SO}_2$ 7:1 (w/w) was allowed to stand at -55°C (5 mm sealed NMR tube) the monosultine **5** was formed slowly. After 2 days at -55°C , 50% of **5** was formed together with <5% of sulfolene **6** and ca. 5% of an unknown compound the ^1H -NMR spectrum of which was not consistent with an isomeric sultine or sulfolene. After 7 days at -55°C , nearly 95% of **1** had reacted. At -45°C , sultine **5** underwent cycloreversion into **1** + SO_2 that reacted slowly to give **6** which was obtained in 85% yield after 24 h at 0°C . The cheletropic addition of a second equivalent of SO_2 to give the bis-sulfolene **7** was a very slow process at 0°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°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 SO₂.

The structures of **5**,⁵ **6**⁶ and **7**⁷ were deduced from their ¹H- and ¹³C-NMR spectra and with the help of double irradiation experiments. In the case of **5** the homoallylic coupling constants ⁵J_{H,H} between protons H-C(3) on one hand, and protons H-C(6) and H-C(8), on the other hand,⁸ 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_e-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.⁹

The selectivities reported here for the reaction of **1** with SO₂ are striking; they rise a number of questions to which we hope to propose answers when further reactions of SO₂ with polyenes analogous to **1** will have been examined.



Figure

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References and Notes

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- Data of **5**: ¹H-NMR (Bruker, ARX 400, CD₂Cl₂/SO₂, -55°C) δ_H: 5.5, 5.2, 5.1, 4.8 (4s, H₂C=C(10), H₂C=C(11)), 4.57 (ddd, ²J=15, ⁵J(H_a-C(6),H_a-C(3))=3, ⁵J(H_a-C(6),H_e-C(3))=2, H_a-C(6)), 4.20 (dd, ²J=15, ⁵J(H_e-C(6),H_a-C(3))=1.0, H_e-C(6)), 3.82 (dd, ³J=2, ⁵J(H_a-C(3),H-C(8))=1.0, H-C(8)), 3.53 (dddd, ²J=17, ⁵J(H_a-C(3),H_a-C(6))=3, ⁵J(H_a-C(3),H_e-C(6)) = ⁵J(H_a-C(3),H-C(8))=1.0, H_a-C(3)), 3.06 (dd, ²J=17, ⁵J(H_a-C(6),H_e-C(3))=2, H_e-C(3)), 2.85 (dd, ³J=6, 2, H-C(9)), 2.28 (d, ²J=10, H_{syn}-C(12)), 1.92 (dd, ²J=10, ³J=6, H_{anti}-C(12)), 0.90 (s, t-Bu), 0.16 & 0.15 (2s, Me₂Si); ¹³C-NMR (100.6 MHz, CD₂Cl₂, -55°C) δ_C: 148.0, 145.0 (2s, C(10), C(11)), 129.4, 127.4 (2s, C(2), C(7)), 109.2, 101.0 (2t, ¹J=160, C(10), C(11)), 83.6 (s, C(11)), 73.3 (d, ¹J=145, C(8)), 59.7 (t, ¹J= 151, C(3)), 52.1 (q, ¹J=142, MeO), 46.3 (d, ¹J=140, C(9)), 44.8 (t, ¹J=140, C(6)), 31.3 (t, ¹J=135, C(12)), 25.3 (q, ¹J=125, t-Bu), 17.7 (s, SiC), -5.1, -5.2 (2q, ¹J=118, Me₂Si).
- Data of **6**: ¹H-NMR (360 MHz, CD₂Cl₂/SO₂, 0°C) δ_H: 5.62, 5.38, 5.22, 4.95 (4s), 4.0-3.9 (m, H_a-C(3), H_a-C(5), H-C(7)), 3.8-3.72 & 3.62-3.60 (2m, H_b-C(3), H_b-C(5)), 3.33 (s, MeO), 2.98 (m, H-C(8)), 2.22 (d, ²J= 10) & 1.93 (dd, ²J= 10, ³J= 6, H₂C(11)), 0.95 (s, t-Bu), 0.20 & 0.15 (2 s, Me₂Si); ¹³C-NMR (100.6 MHz, CD₂Cl₂/SO₂, 0°C) δ_C: 147.4, 145.3, 139.9, 128.6 (4s), 109.7 (t, 2C, ¹J=159), 84.3 (s, C(1)), 72.4 (d, ¹J= 146, C(7)), 58.8 (t, ¹J= 143, C(3)), 55.7 (t, ¹J=157, C(5)), 52.6 (q, ¹J=143, MeO), 47.4 (d, ¹J=141, C(8)), 31.8 (t, ¹J=135, C(11)), 25.8 (q, ¹J=125), 18.3 (s), -4.61 & -4.74 (2 q, ¹J=119).
- Data of **7**: ¹H-NMR (360 MHz, SO₂/CD₂Cl₂, 20°C) δ_H: 4.1 (m, H-C(7)), 4.0-3.75 (m, 8H, H₂C(3), H₂C(5), H₂C(10), H₂C(12)), 3.35 (s, MeO), 3.08 (m, H-C(8)), 2.58 (dd, ²J= 10, ³J= 5) & 2.45 (d, ²J= 10, H₂C(14)), 0.90 (s, t-Bu), 0.16, 0.15 (2s, Me₂Si); ¹³C-NMR (100.6 MHz, SO₂/CD₂Cl₂, 20°C) δ_C: 125.5 (s, C(2), C(4)), 115.6, 113.9 (2s, C(6), C(9)), 70.9 (s, C(1)), 65.3 (d, ¹J=143, C(7)), 58.3, 57.0, 56.8, 56.1 (4t, ¹J=146), 52.9 (q, ¹J=143, MeO), 47.2 (d, ¹J=144, C(8)), 40.8 (t, ¹J=138, C(14)), 26.1 (q, ¹J=125), 18.7 (s), -4.5, -4.6 (2q).
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