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Homocheletropic Addition of Sulfur Dioxide to 1,4-Dienes. Competition between Cheletropic and Homocheletropic Additions of Polyenes

Jean-Michel Roulet, Brigitte Deguin, and Pierre Vogel*

Section de Chimie de l'Université
2, rue de la Barre, CH 1005 Lausanne, Switzerland

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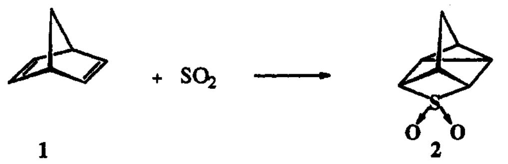
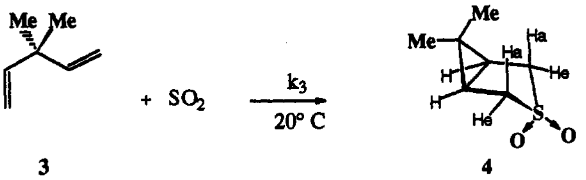
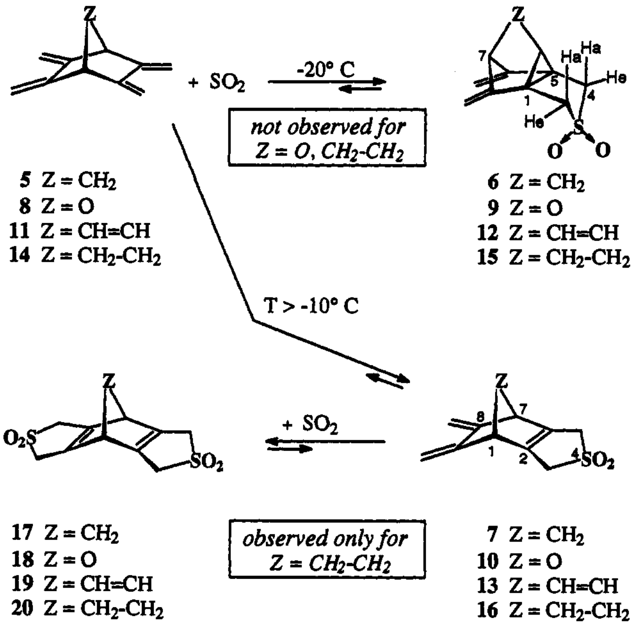
Homoconjugated dienes can be rearranged into conjugated 1,3-dienes in the presence of SO_2 via ene reactions.[1,2] In the case of norbornadiene (**1**), which cannot undergo ene reactions with SO_2, De Lucchi and Lucchini[3] reported that it adds to SO_2 in a ($\omega 2_s + \pi 2_s + \pi 2_s$) fashion[4] to give the corresponding sulfolane **2**. In our hands, mixtures of **1** and SO_2 led only to polymeric material, unless 2,6-di-*tert*-butyl-*p*-cresol was added to the reaction mixture (33% yield of **2** after 2 days at 25 °C). We report here that the homocheletropic addition of SO_2 is not restricted only to norbornadiene and that it can compete with the usual cheletropic addition ($\omega 2_s + \pi 4_s$)[4] when SO_2 is allowed to react with polyenes containing 1,3-diene as well as 1,4-diene moieties.[5]



When 3,3-dimethylpenta-1,4-diene (**3**)[6] was mixed with 12–13 equiv of SO_2 in CH_2Cl_2, an 81% yield of sulfolane **4**[7] was obtained after 8 days at 23 °C. Kinetic measurements gave a second-order rate constant k_3 (296 K) = $1.51 \times 10^{-7} \pm 1.3 \times 10^{-9}$ $dm^3\ mol^{-1}\ s^{-1}$ for reaction **3** + $SO_2 \rightarrow$ **4**. In the presence of CF_3COOH (0.6 equiv) or $BF_3 \cdot Et_2O$ (0.8 equiv), the rate constants k_3(CF_3COOH, 296 K) = $2.8 \times 10^{-7} \pm 8.7 \times 10^{-9}$ $dm^3\ mol^{-1}\ s^{-1}$ and k_3($BF_3 \cdot Et_2O$, 298 K) = $7.26 \times 10^{-7} \pm 8.7 \times 10^{-9}$ $dm^3\ mol^{-1}\ s^{-1}$, respectively, were measured. This relatively weak accelerating effect due to the protic or Lewis acid sharply contrasts with the strong acid catalytic effect observed for the hetero-Diels–Alder additions of SO_2 to simple 1,3-dienes at low temperature.[8] The rate of the homocheletropic addition **3** + $SO_2 \rightarrow$ **4** was not affected by the presence of a radical scavenger such as 2,6-di-*tert*-butyl-*p*-cresol, thus ruling out the hypothesis that this reaction implies the formation of radicals or diradicals in the rate-determining step.



Scheme 1



When 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**5**)[9,10] was mixed with SO_2 (purified on alkaline alumina (I)) in CD_2Cl_2 (sealed NMR tube, C_6H_6 as internal reference), the sulfolane **6**[11] was formed as a single product at –20 °C (Scheme 1). A second-order rate constant k_5(253 K) = $1.59 \times 10^{-5} \pm 2.6 \times 10^{-7}$ $dm^3\ mol^{-1}\ s^{-1}$ was measured. At 0 °C, **6** underwent slow cycloreversion into **5** + SO_2 and then formed sulfolene **7**.[12] In this case, the homocheletropic addition **5** + $SO_2 \rightarrow$ **6** is kinetically favored but thermodynamically disfavored compared with the cheletropic addition **5** + $SO_2 \rightarrow$ **7**. At higher temperatures, **6** and **7** were equilibrated with tetraene **5**, showing that **6** and **7** had similar stabilities (ratio of **6**/**7**, 1:4).

When 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**8**)[10,13,14] was mixed with a large excess of SO_2, no product **9** resulting from a homocheletropic addition could be detected between –30 °C and 30 °C. Above –10 °C, slow formation of sulfolene **10**[15] was observed.

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(1) Rogic, M.; Masilamani, D. *J. Am. Chem. Soc.* **1977**, *99*, 5219. See also: Capozzi, G.; Lucchini, V.; Marcuzzi, F.; Melloni, G. *Tetrahedron Lett.* **1980**, *21*, 3289.

(2) We have found that the reaction of SO_2 with penta-1,4-diene in CH_2Cl_2 gives mixtures of (*E*)- and (*Z*)-penta-2,4-dienesulfinic acid and (*E*)- and (*Z*)-piperylene.

(3) De Lucchi, O.; Lucchini, V. *J. Chem. Soc., Chem. Commun.* **1982**, 1105.

(4) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970. Turk, S. D.; Cobb, R. L. In *1,4-Cycloadditon Reactions*; Hamer, J., Ed.; Academic Press: New York, 1967; p 13. Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

(5) For three component reactions of SO_2, see, e.g.: Decazes, J. M.; Luche, J.-L.; Kagan, H. B.; Parthasarathy, R.; Ohrt, J. *Tetrahedron Lett.* **1972**, 3633. Belluš, D. *Helv. Chem. Acta* **1975**, *58*, 2509.

(6) Eilbracht, P.; Acker, M.; Totzauer, W. *Chem. Ber.* **1983**, *116*, 238.

(7) Data for **4**: white crystals; mp 75–76 °C; ^1H NMR (250 MHz, CD_3CN) δ_H 3.31 (m, 2 H, ^2J = 14.2 Hz, ^3J = 6.8 Hz, ^5J = 1.4 Hz, H(2e), H(4e)), 2.60 (m, 2 H, ^2J = 14.2 Hz, H(2a), H(4a)), 1.57 (m, 2 H, ^3J = 6.8 Hz, ^5J = 1.4 Hz, H(1), H(5)), 1.14, 0.97 (2 s, 6 H, 2 Me); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ_C 50.6 (t, ^1J(C,H) = 143 Hz, C(2), C(4)), 26.2 (q, ^1J(C,H) = 127 Hz, Me equatorial), 22.2 (d, ^1J(C,H) = 173 Hz, C(1), C(5)), 21.7 (s, C(6)), 13.7 (q, ^1J(C,H) = 127 Hz, Me axial).

(8) Deguin, B.; Vogel, P. *J. Am. Chem. Soc.* **1992**, *114*, 9210.

(9) Florey, A.; Vogel, P. *Helv. Chem. Acta* **1975**, *58*, 1488; Pilet, O.; Vogel, P. *Ibid.* **1981**, *64*, 2563.

(10) Vogel, P. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1989; Vol. I, pp 201–355.

(11) Data for **6**: mp 91° C dec; ^1H NMR (400 MHz, CD_2Cl_2, SO_2, –20° C) δ_H 4.95, 4.76 (2 s, 4H, $H_2C{=}C(6)$, $H_2C{=}C(10)$), 3.76 (dm, 2H, ^2J = 13.7 Hz, H(2e), H(4e)), 3.09 (dm, 2H, ^2J = 13.7 Hz, H(2a), H(4a)), 2.86 (t, 1H, ^3J = 1.4 Hz, H(7)), 2.31 (t, 1H, ^3J = 1.0 Hz, H(9)), 1.84 (dd, 2 H, ^3J = 1.4 Hz, ^3J = 1.0 Hz, H(8)); ^{13}C NMR (100.61 MHz, CD_2Cl_2, SO_2, –20 °C) δ_C 151.1 (s, C(6), C(10)), 100.1 (t, ^1J(C,H) = 159 Hz, $H_2C{=}C(6)$, $H_2C{=}C(10)$), 50.5 (t, ^1J(C,H) = 144 Hz, C(2), C(4)), 44.4 (d, ^1J(C,H) = 155 Hz, C(7)), 35.9 (t, ^1J(C,H) = 137 Hz, C(8)), 35.6 (d, ^1J(C,H) = 181 Hz, C(9)), 34.7 (s, C(1), C(5)).

(12) Data for **7**: mp 96 °C dec; ^1H NMR (250 MHz, $CDCl_3$) δ_H 5.26, 5.03 (2 s, 4H, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 3.92 (dm, 2H, ^2J = 16.4 Hz, H(3e), H(5e)), 3.65 (dm, 2H, ^2J = 16.4 Hz, H(3a), H(5a)), 3.44 (t, 2H, ^3J = 1.7 Hz, H(1), H(7)), 2.01 (dt, 1H, ^2J = 8.7 Hz, ^3J = 1.7 Hz, H(10)), 1.80 (dt, 1H, ^3J = 1.7 Hz, ^2J = 8.7 Hz, H(10)); ^{13}C NMR (100.61 MHz, CD_2Cl_2) δ_C 147.2 (s, C(8), C(9)), 140.9 (s, C(2), C(6)), 104.6 (t, ^1J(C,H) = 159 Hz, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 56.4 (t, ^1J(C,H) = 145 Hz, C(3), C(5)), 51.7 (d, ^1J(C,H) = 145 Hz, C(1), C(7)), 49.3 (t, ^1J(C,H) = 137 Hz, C(10)).

(13) Vogel, P.; Florey, A. *Helv. Chem. Acta* **1974**, *57*, 200. Mahaim, C.; Carrupt, P.-A.; Hagenbuch, J.-P.; Florey, A.; Vogel, P. *Ibid.* **1980**, *63*, 1149.

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Between −40 °C and 25 °C, SO_2 was added to 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**11**)[10,16] to give a 1:1 mixture of sulfolane **12**[17] and sulfolene **13**.[18] This product ratio and the rate of this reaction ($k_{11}(253\ \mathrm{K}) = 4.20 \times 10^{-6} \pm 6.3 \times 10^{-8}$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$) were not affected significantly by the presence of 2,6-di-*tert*-butyl-*p*-cresol or CF_3COOH. Above 25 °C, **12** was slowly isomerized into **13** via homocheletropic elimination, giving **11** + SO_2, which underwent cheletropic addition to **13**, **13** being more stable than **12**. Heating of **13** above 100 °C led to elimination of SO_2 and recovery of pentaene **11**. In contrast, tetraene **14**[10,16] did not to give any trace of the expected sulfolane **15** when treated with various amounts of SO_2 between −40 °C and 40 °C. The sulfolene **16** was formed instead (k_{14} (253 K) $= 1.75 \times 10^{-5} \pm 5.5 \times 10^{-7}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$), which added, above −20 °C, a second equivalent of SO_2 to give the bis-sulfolene **20**.[19] Below −65 °C, **14** was equilibrated slowly with a 3:2 mixture of two diastereomeric sultines resulting from the hetero-Diels–Alder addition of SO_2.[8]

In contrast with the facile reaction **16** + $SO_2 \rightarrow$ **20**, no trace of the corresponding bis-sulfolenes **17**, **18**, and **19** resulting from the cheletropic additions of SO_2 to **7**, **10**, and **13** could be detected between 0 °C and 100 °C when polyenes **5**, **8**, and **11**, respectively, were allowed to react with SO_2 for several days. This is probably due to the fact that the corresponding bis-sulfolenes **17**, **18**, and **19** are unstable above 0 °C with respect to the products of cheletropic elimination because of the extra strain of bicyclo[2.2.1]hepta-2,5-diene (**17**), 7-oxabicyclo[2.2.1]hepta-2,5-diene (**18**), and barrelene systems (**19**) compared with bicyclo[2.2.2]octa-2,5-diene derivatives such as **20**.[10,20]

The homocheletropic additions **5** + $SO_2 \rightarrow$ **6** and **11** + $SO_2 \rightarrow$ **12** (occurring at −20 °C) were significantly faster than reaction **3** + $SO_2 \rightarrow$ **4** (occurring at 20 °C). This might be explained in terms of an electronic factor: the olefinic moieties in polyenes **5** and **11** being part of *s-cis*-butadiene units are more polarizable than those of the simple 1,4-diene **3**. Differential electronic effects could also be responsible for the competition between the cheletropic and homocheletropic additions of SO_2 to polyenes **5**, **8**, **11**, and **14**. Alternatively, geometrical factors such as the angle between the two reacting olefinic moieties and the distance between them could also be decisive.

Work is underway in our laboratory to put these hypotheses on firmer ground. For the moment it is interesting to realize that a simple compound such as SO_2 has a wealth of chemistry to offer as a cycloaddend.

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Supplementary Material Available: Preparations and characteristics of sulfolanes **6**, **12**, sulfolenes **7**, **10**, **13**, **16**, bissulfolene **20**, and sultines **21**, **21′** resulting from the hetero-Diels–Alder addition of SO_2 to **14**; kinetic measurements of the cycloaddition of SO_2 on **3** and **11**, (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[14] For synthetic applications of this tetraene, see, e.g.: Tamariz, J.; Vogel, P. *Tetrahedron* **1984**, *40*, 4549. Tornare, J.-M.; Vogel, P. *Helv. Chem. Acta* **1985**, *68*, 1069. Ashton, P. R.; Isaacs, N. S.; Kohnke, F. H.; Mathias, J. P.; Stoddart, J. F. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1258. Ashton, P. R.; Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Raymo, F. M.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 5422.

[15] Data for **10**: mp 103 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H 5.38, 5.18 (2 s, 4 H, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 5.27 (m, 2 H, H(1), H(7)), 4.05 (dm, 2 H, ^2J = 16.5 Hz, H(3e), H(5e)), 3.72 (dm, 2 H, ^2J = 16.5 Hz, H(3a), H(5a)); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ_C 141.0 (s, C(8), C(9)), 140.4 (s, C(2), C(6)), 104.5 (t, ^1J(C,H) = 161 Hz, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 83.0 (d, ^1J(C,H) = 163 Hz, C(1), C(7)), 55.1 (t, ^1J(C,H) = 144 Hz, C(3), C(5)).

[16] Chollet, A.; Wismer, M.; Vogel, P. *Tetrahedron Lett.* **1976**, *47*, 4271.

[17] Pure sulfolane **12** was obtained by allowing **13** to react with *N*-phenyltriazolinedione at −20 °C. The Diels–Alder adduct so obtained was readily separated from **12** by column chromatography on silica gel. Data for **12**: mp 122 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H 6.13 (ddd, 1H, ^3J = 7.8, 7.0 Hz, ^4J = 2.8 Hz, H(8)), 5.98 (ddd, 1H, ^3J = 7.8, 5.5 Hz, ^4J = 1.5 Hz, H(9)), 5.02, 4.70 (2 s, 4 H, $H_2C{=}C(6)$, $H_2C{=}C(11)$), 3.78 (d, 2H, ^2J = 13.5 Hz, H(2e), H(4e)), 3.48 (d, 1H, ^3J = 7.0 Hz, ^4J = 1.5 Hz, H(7)), 3.23 (d, 2H, ^2J = 13.5 Hz, H(2a), H(4a)), 2.62 (dd, 1H, ^3J = 5.5 Hz, ^4J = 2.8 Hz, H(10)); ^{13}C NMR (100.61 MHz, CD_2Cl_2) δ_C 145.2 (s, C(6), C(11)), 129.8 (d, ^1J(C,H) = 173 Hz, C(8)), 122.2 (d, ^1J(C,H) = 169 Hz, C(9)), 102.8 (t, ^1J(C,H) = 159 Hz, $H_2C{=}C(6)$, $H_2C{=}C(11)$), 53.7 (t, ^1J(C,H) = 143 Hz, C(2), C(4)), 50.2 (d, ^1J(C,H) = 134 Hz, C(7)), 39.7 (d, ^1J(C,H) = 171 Hz, C(10)), 36.6 (s, C(1), C(5)).

[18] Data for **13**: mp > 145 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ_C 6.48 (dd, 2H, ^3J = 4.5 Hz, ^4J = 3.2 Hz, H(10), H(11)), 5.20, 4.93 (2 s, 4 H, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 4.13 (dd, 2H, ^3J = 4.5 Hz, ^4J = 3.2 Hz, H(1), H(7)), 3.92 (s, 4 H, H(3), H(5)); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ_C 141.5 (s, C(8), C(9)), 134.8 (s, C(2), C(6)), 133.3 (d, ^1J(C,H) = 173 Hz, C(10), C(11)), 104.4 (t, ^1J(C,H) = 159 Hz, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 57.9 (t, ^1J(C,H) = 144 Hz, C(3), C(5)), 48.9 (d, ^1J(C,H) = 144 Hz, C(1), C(7)).

[19] Data for **16**: mp 115 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ_H 5.23, 4.84 (2 s, 4 H, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 3.91 (s, 4 H, H(3), H(5)), 3.27 (br s, 2 H, H(1), H(7)), 1.79, 1.56 (2 m, 4 H, H(10), H(11)); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ_C 144.7 (s, C(8), C(9)), 133.9 (s, C(2), C(6)), 104.5 (t, ^1J(C,H) = 159 Hz, $H_2C{=}C(8)$, $H_2C{=}C(9)$), 57.8 (t, ^1J(C,H) = 144 Hz, C(3), C(5)), 42.7 (d, ^1J(C,H) = 140 Hz, C(1), C(7)), 26.1 (t, ^1J(C,H) = 134 Hz, C(10), C(11)). Data for **20**: mp > 145 °C dec; ^{1}H NMR (250 MHz, CD_3CN) δ_H 3.87 (br s, 8 H, H(3), H(5), H(9), H(11)), 3.70 (br s, 2 H, H(1), H(7)), 1.52 (s, 4 H, H(13), H(14)); ^{13}C NMR (100.61 MHz, CD_3CN) δ_C 135.3 (s, C(2), C(6), C(8), C(12)), 57.8 (t, ^1J(C,H) = 145 Hz, C(3), C(5), C(9), C(11)), 38.5 (d, ^1J(C,H) = 144 Hz, C(1), C(7)), 25.6 (t, ^1J(C,H) = 128 Hz, C(13), C(14)).

[20] Turner, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 3586. Jensen, J. L. *Prog. Phys. Org. Chem.* **1976**, *12*, 189.