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

Jean-Michel Roulet, Brigitte Deguin, Pierre Vogel

► To cite this version:

Jean-Michel Roulet, Brigitte Deguin, Pierre Vogel. Homochelotropic Addition of Sulfur Dioxide to 1,4-Dienes. Competition between Cheletropic and Homochelotropic Additions of Polyenes. Journal of the American Chemical Society, 1994, 116, pp.3639-3640. hal-01927363

HAL Id: hal-01927363

<https://hal.science/hal-01927363>

Submitted on 19 Nov 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Homoconjugated dienes can be rearranged into conjugated 1,3-dienes in the presence of SO₂ via ene reactions.^{1,2} In the case of norbornadiene (1), which cannot undergo ene reactions with SO₂, De Lucchi and Lucchini³ reported that it adds to SO₂ in a ($\omega_2 + \pi_2 + \pi_2$) fashion⁴ to give the corresponding sulfolane 2. In our hands, mixtures of 1 and SO₂ 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 SO₂ is not restricted only to norbornadiene and that it can compete with the usual cheletropic addition ($\omega_2 + \pi_4$)⁴ when SO₂ 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 SO₂ in CH₂Cl₂, an 81% yield of sulfolane 4⁷ was obtained after 8 days at 23 °C. Kinetic measurements gave a

second-order rate constant k_3 (296 K) = $1.51 \times 10^{-7} \pm 1.3 \times 10^{-9}$ dm³ mol⁻¹ s⁻¹ for reaction 3 + SO₂ → 4. In the presence of CF₃-COOH (0.6 equiv) or BF₃·Et₂O (0.8 equiv), the rate constants k_3 (CF₃COOH, 296 K) = $2.8 \times 10^{-7} \pm 8.7 \times 10^{-9}$ dm³ mol⁻¹ s⁻¹ and k_3 (BF₃·Et₂O, 298 K) = $7.26 \times 10^{-7} \pm 8.7 \times 10^{-9}$ dm³ mol⁻¹ s⁻¹, respectively, were measured. This relatively weak accelerating effect due to the protic or Lewis acid sharply contrasts with the

Scheme 1

strong acid catalytic effect observed for the hetero-Diels–Alder additions of SO₂ to simple 1,3-dienes at low temperature.⁸ The rate of the homocheletropic addition 3 + SO₂ → 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.

When 2,3,5,6-tetramethyldienebicyclo[2.2.1]heptane (5)^{9,10} was mixed with SO₂ (purified on alkaline alumina (I)) in CD₂Cl₂ (sealed NMR tube, C₆H₆ as internal reference), the sulfolane 6¹¹ was formed as a single product at -20 °C (Scheme 1). A second-order rate constant k_5 (253 K) = $1.59 \times 10^{-5} \pm 2.6 \times 10^{-7}$ dm³ mol⁻¹ s⁻¹ was measured. At 0 °C, 6 underwent slow cycloreversion into 5 + SO₂ and then formed sulfolane 7.¹² In this case, the homocheletropic addition 5 + SO₂ → 6 is kinetically favored but thermodynamically disfavored compared with the cheletropic addition 5 + SO₂ → 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-tetramethyldiene-7-oxabicyclo[2.2.1]heptane (8)^{10,13,14} was mixed with a large excess of SO₂, no product 9 resulting from a homocheletropic addition could be detected between -30 °C and 30 °C. Above -10 °C, slow formation of sulfolane 10¹⁵ was observed.

(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 SO₂ with penta-1,4-diene in CH₂-Cl₂ gives mixtures of (*E*)- and (*Z*)-penta-2,4-dienesulfonic 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-Cycloaddition 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 SO₂, see, e.g.: Decazes, J. M.; Luche, J.-L.; Kagan, H. B.; Parthasarathy, R.; Ohrt, J. *Tetrahedron Lett.* **1972**, 3633. Beiluss, 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, CD₃CN) δ 3.31 (m, 2H, ²J = 14.2 Hz, ³J = 6.8 Hz, ⁴J = 1.4 Hz, H(2e), H(4e)), 2.60 (m, 2H, ²J = 14.2 Hz, H(2a), H(4a)), 1.57 (m, 2H, ²J = 6.8 Hz, ³J = 1.4 Hz, H(1), H(5)), 1.14, 0.97 (2 s, 6 H, 2 Me); ¹³C NMR (100.61 MHz, CDCl₃) δ 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. 1, pp 201–355.

(11) Data for 6: mp 91 °C dec; ¹H NMR (400 MHz, CD₂Cl₂, SO₂, -20 °C) δ 4.95, 4.76 (2 s, 4H, H₂C=C(6), H₂C=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, ²J = 1.4 Hz, H(7)), 2.31 (t, 1H, ²J = 1.0 Hz, H(9)), 1.84 (dd, 2H, ²J = 1.4 Hz, ³J = 1.0 Hz, H(8)); ¹³C NMR (100.61 MHz, CD₂Cl₂, SO₂, -20 °C) δ 151.1 (s, C(6), C(10)), 100.1 (t, ¹J(C,H) = 159 Hz, H₂C=C(6), H₂C=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, CDCl₃) δ 5.26, 5.03 (2 s, 4H, H₂C=C(8), H₂C=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, ²J = 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, ²J = 1.7 Hz, ³J = 8.7 Hz, H(10)), ¹³C NMR (100.61 MHz, CD₂Cl₂) δ 147.2 (s, C(8), C(9)), 140.9 (s, C(2), C(6)), 104.6 (t, ¹J(C,H) = 159 Hz, H₂C=C(8), H₂C=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.

Between $-40\text{ }^{\circ}\text{C}$ and $25\text{ }^{\circ}\text{C}$, SO_2 was added to 5,6,7,8-tetra-methylidenebicyclo[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 ($k_{11}(253\text{ K}) = 4.20 \times 10^{-6} \pm 6.3 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) were not affected significantly by the presence of 2,6-di-*tert*-butyl-*p*-cresol or CF_3COOH . Above $25\text{ }^{\circ}\text{C}$, **12** was slowly isomerized into **13** via homochelotropic elimination, giving **11** + SO_2 , which underwent cheletropic addition to **13**, **13** being more stable than **12**. Heating of **13** above $100\text{ }^{\circ}\text{C}$ 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 $-40\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$. The sulfolene **16** was formed instead ($k_{14}(253\text{ K}) = 1.75 \times 10^{-5} \pm 5.5 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), which added, above $-20\text{ }^{\circ}\text{C}$, a second equivalent of SO_2 to give the bis-sulfolene **20**.¹⁹ Below $-65\text{ }^{\circ}\text{C}$, **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 $\text{16} + \text{SO}_2 \rightarrow \text{20}$, 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

(14) For synthetic applications of this tetraene, see, e.g.: Tamariz, J.; Vogel, P. *Tetrahedron* **1984**, *40*, 4549. Tornare, J.-M.; Vogel, P. *Helv. Chim. 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.; Gluffrida, 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 $103\text{ }^{\circ}\text{C}$ dec; ^1H NMR (250 MHz, CDCl_3) δ_{H} 5.38, 5.18 (2 s, 4 H, $\text{H}_2\text{C}=\text{C}(8)$, $\text{H}_2\text{C}=\text{C}(9)$), 5.27 (m, 2 H, H(1), H(7)), 4.05 (dm, 2 H, $^3J = 16.5\text{ Hz}$, H(3e), H(5e)), 3.72 (dm, 2 H, $^3J = 16.5\text{ Hz}$, 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, $^1J(\text{C,H}) = 161\text{ Hz}$, $\text{H}_2\text{C}=\text{C}(8)$, $\text{H}_2\text{C}=\text{C}(9)$), 83.0 (d, $^1J(\text{C,H}) = 163\text{ Hz}$, C(1), C(7)), 55.1 (t, $^1J(\text{C,H}) = 144\text{ Hz}$, 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 $-20\text{ }^{\circ}\text{C}$. The Diels-Alder adduct so obtained was readily separated from **12** by column chromatography on silica gel. Data for **12**: mp $122\text{ }^{\circ}\text{C}$ dec; ^1H NMR (250 MHz, CDCl_3) δ_{H} 6.13 (ddd, 1H, $^3J = 7.8$, $^4J = 7.0\text{ Hz}$, $^4J = 2.8\text{ Hz}$, H(8)), 5.98 (ddd, 1H, $^3J = 7.8$, $^5J = 5.5\text{ Hz}$, $^4J = 1.5\text{ Hz}$, H(9)), 5.02, 4.70 (2 s, 4 H, $\text{H}_2\text{C}=\text{C}(6)$, $\text{H}_2\text{C}=\text{C}(11)$), 3.78 (d, 2H, $^2J = 13.5\text{ Hz}$, H(2e), H(4e)), 3.48 (d, 1H, $^3J = 7.0\text{ Hz}$, $^4J = 1.5\text{ Hz}$, H(7)), 3.23 (d, 2H, $^2J = 13.5\text{ Hz}$, H(2a), H(4a)), 2.62 (dd, 1H, $^3J = 5.5\text{ Hz}$, $^4J = 2.8\text{ Hz}$, H(10)); ^{13}C NMR (100.61 MHz, CD_2Cl_2) δ_{C} 145.2 (s, C(6), C(11)), 129.8 (d, $^1J(\text{C,H}) = 173\text{ Hz}$, C(8)), 122.2 (d, $^1J(\text{C,H}) = 169\text{ Hz}$, C(9)), 102.8 (t, $^1J(\text{C,H}) = 159\text{ Hz}$, $\text{H}_2\text{C}=\text{C}(6)$, $\text{H}_2\text{C}=\text{C}(11)$), 53.7 (t, $^1J(\text{C,H}) = 143\text{ Hz}$, C(2), C(4)), 50.2 (d, $^1J(\text{C,H}) = 134\text{ Hz}$, C(7)), 39.7 (d, $^1J(\text{C,H}) = 171\text{ Hz}$, C(10)), 36.6 (s, C(1), C(5)).

(18) Data for **13**: mp $> 145\text{ }^{\circ}\text{C}$ dec; ^1H NMR (250 MHz, CDCl_3) δ_{C} 6.48 (dd, 2H, $^3J = 4.5\text{ Hz}$, $^4J = 3.2\text{ Hz}$, H(10), H(11)), 5.20, 4.93 (2 s, 4 H, $\text{H}_2\text{C}=\text{C}(8)$, $\text{H}_2\text{C}=\text{C}(9)$), 4.13 (dd, 2H, $^3J = 4.5\text{ Hz}$, $^4J = 3.2\text{ Hz}$, 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, $^1J(\text{C,H}) = 173\text{ Hz}$, C(10), C(11)), 104.4 (t, $^1J(\text{C,H}) = 159\text{ Hz}$, $\text{H}_2\text{C}=\text{C}(8)$, $\text{H}_2\text{C}=\text{C}(9)$), 57.9 (t, $^1J(\text{C,H}) = 144\text{ Hz}$, C(3), C(5)), 48.9 (d, $^1J(\text{C,H}) = 144\text{ Hz}$, C(1), C(7)).

between $0\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$ 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 $0\text{ }^{\circ}\text{C}$ 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 homochelotropic additions $\text{5} + \text{SO}_2 \rightarrow \text{6}$ and $\text{11} + \text{SO}_2 \rightarrow \text{12}$ (occurring at $-20\text{ }^{\circ}\text{C}$) were significantly faster than reaction $\text{3} + \text{SO}_2 \rightarrow \text{4}$ (occurring at $20\text{ }^{\circ}\text{C}$). 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 homochelotropic 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.

Acknowledgment. We are grateful to the Swiss National Science Foundation, the Fonds Herbette (Lausanne), and F. Hoffmann-La Roche AG & Co. (Basel) for financial support.

Supplementary Material Available: Preparations and characteristics of sulfolanes **6**, **12**, sulfolenes **7**, **10**, **13**, **16**, bisulfolene **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.

(19) Data for **16**: mp $115\text{ }^{\circ}\text{C}$ dec; ^1H NMR (250 MHz, CDCl_3) δ_{H} 5.23, 4.84 (2 s, 4 H, $\text{H}_2\text{C}=\text{C}(8)$, $\text{H}_2\text{C}=\text{C}(9)$), 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, $^1J(\text{C,H}) = 159\text{ Hz}$, $\text{H}_2\text{C}=\text{C}(8)$, $\text{H}_2\text{C}=\text{C}(9)$), 57.8 (t, $^1J(\text{C,H}) = 144\text{ Hz}$, C(3), C(5)), 42.7 (d, $^1J(\text{C,H}) = 140\text{ Hz}$, C(1), C(7)), 26.1 (t, $^1J(\text{C,H}) = 134\text{ Hz}$, C(10), C(11)). Data for **20**: mp $> 145\text{ }^{\circ}\text{C}$ dec; ^1H 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, $^1J(\text{C,H}) = 145\text{ Hz}$, C(3), C(5), C(9), C(11)), 38.5 (d, $^1J(\text{C,H}) = 144\text{ Hz}$, C(1), C(7)), 25.6 (t, $^1J(\text{C,H}) = 128\text{ Hz}$, 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.