

**Oxidation of Olefins by Potassium Permanganate.
¹⁸O-Labeling Experiments and Mechanism of the
 Oxidation of 1,5-Hexadiene. Evidence for a Manganese
 Intermediate with Coordination Number Greater Than
 Four†**

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The oxidation of an olefin by potassium permanganate in aqueous media proceeds via a hypomanganate or manganate ester intermediate, which may undergo hydrolysis to an α -glycol¹ or oxidative hydrolysis to an α -ketol,² depending on the pH. Since the hydrolytic steps of these reactions occur with fission of Mn-O bonds,³ it might be expected that these steps lead to manganese species with coordination number greater than four, analogous to the tetrahedral intermediate of organic ester hydrolysis. This communication provides indirect evidence for the presence of a transient penta- or hexacoordinated species during the permanganate oxidation of 1,5-hexadiene to the 2,5-anhydro tetrol **1**, *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran.^{4,5}

Repetition of Klein and Rojahn's oxidation of 1,5-hexadiene (aqueous acetone, -10 °C, pH 6^{4,16}) led to **1** in the reported ca. 20% yield and also the previously unreported ketol **2**¹⁷ (8%). The

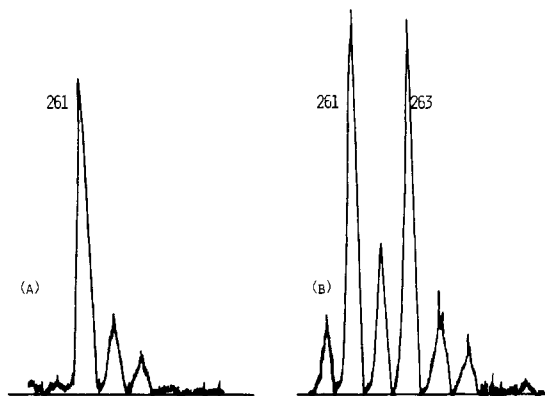


Figure 1. (A) *m/e* 261 region of the mass spectrum of **4**. (B) *m/e* 261 region of the mass spectrum of **4** prepared by oxidation of 1,5-hexadiene with potassium permanganate in a solvent containing 92% enriched H₂¹⁸O. The data were obtained on a Finnigan 31000 GC/MS instrument, by using a 5-ft glass column packed with 3% OV1 Chromosorb W-HP and temperature programming from 100 to 150 °C at 6 °C/min.

Table I. Calculated and Experimentally Observed Mass Spectrum of **4** Prepared by Oxidation of 1,5-Hexadiene with ¹⁸O-Labeled Potassium Permanganate^a

<i>m/e</i>	calcd for incorp of two O, %	calcd for incorp of three O, %	found, %
261	59.8	48.3	54 ^b
263	31.9	34.7	34
265	8.3	13.1	10
267	0	3.9	2

^a The percentage of species containing 0, 1, 2, 3 and 4 atoms of ¹⁸O are, respectively, 39.2, 35.7, 15.7, 6.9 and 2.2. ^b Average of six determinations. The error is $\pm 1\%$.

latter is the "normal" product of the permanganate oxidation of a terminal olefin under these reaction conditions.² Its formation indicates² that the manganate ester **3** is present in the reaction mixture and can react with water, inter alia, at the C2-H bond, as shown (Scheme I).

The bis(trimethylsilyl) ether **4** exhibited an *M* + 1 peak at *m/e* 277 under CI-MS conditions and an *M* - 15 peak¹⁸ at *m/e* 261 under EI-MS conditions. In both cases, the fragmentation shown in **4** was observed, leading to a peak at *m/e* 144, which retains one of the hydroxyl oxygens. These observations provided the analytical basis for an examination of the origins of the oxygen atoms of the anhydro tetrol **1**.¹⁹

Figure 1 shows the *m/e* 261 region of the electron-impact mass spectra of **4** and the compound prepared in the presence of 92% enriched H₂¹⁸O. It is evident that one of the oxygen atoms of the product is derived from the solvent. It is also evident, from the relative intensities of the *m/e* 261 and 263 peaks of Figure 1B,

(18) Such a peak is commonly observed in the mass spectra of trimethylsilyl ethers. See, e.g., DeJongh, D. C.; Radford, T.; Hribar, J. D.; Hanessian, S.; Bieber, M.; Dawson, G.; Sweeley, C. C. *J. Am. Chem. Soc.* **1969**, *91*, 1728-1740.

(19) It is known that hypomanganate and manganate undergo rapid oxygen exchange with water in alkaline media²⁰ and both oxyanions are in equilibrium with permanganate by a combination of oxidation²¹ and/or electron transfer.²² This leads to some exchange of permanganate with the solvent in the course of olefin hydroxylation at pH 12.³ Although such exchange was expected to be less important at pH 6, because of the much shorter lifetimes of the lower valence states at the lower pH, it was, nevertheless, desirable to check this point. Therefore, cyclohexene, a "normal" olefin, was oxidized to adipoin² under Klein and Rojahn's conditions for the oxidation of **3**, in a mixture of acetone (90%) and 12.5% enriched H₂¹⁸O (10%), and the product was examined by mass spectrometry. No incorporation of ¹⁸O was observed.

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† Dedicated to Professor Raymond U. Lemieux, on the occasion of his 60th birthday.

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(2) See: Wolfe, S.; Ingold, C. F.; Lemieux, R. U. *J. Am. Chem. Soc.* **1981**, *103*, preceding paper in this issue.

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(4) Klein, E.; Rojahn, W. *Tetrahedron* **1965**, *21*, 2353-2358.

(5) There is considerable evidence that the manganese ester intermediate(s) of olefin oxidation can react intramolecularly with a neighboring double bond. Thus, although most 1,4-dienes are converted by permanganate to a mixture of unsaturated cis diols, and *cis*-syn-*cis* and *cis*-anti-*cis* tetrols⁶ and methyl sandaracopimarate undergoes normal periodate-permanganate oxidation,^{7,8} methyl pimarate, the C-13-epimer of this latter compound, affords an epoxy ketol as the primary product.⁹ The oxidation of 1,3-dienes leads, invariably, to an all-*cis* anhydro tetrol. For example, 1,3-cyclohexadiene,⁹ cyclopentadiene,⁹ ergosterol,¹⁰ and abietic acid¹¹ are oxidized to 1,2-anhydro tetrols; levopimaric acid gives a 1,4-anhydro tetrol;¹² and occidantalol yields a 2,3-anhydro tetrol.¹³ The oxidation of 1,5-dienes⁴ leads to 2,5-anhydro tetrols, and these are formed by *cis* oxygenation of both double bonds.^{14,15}

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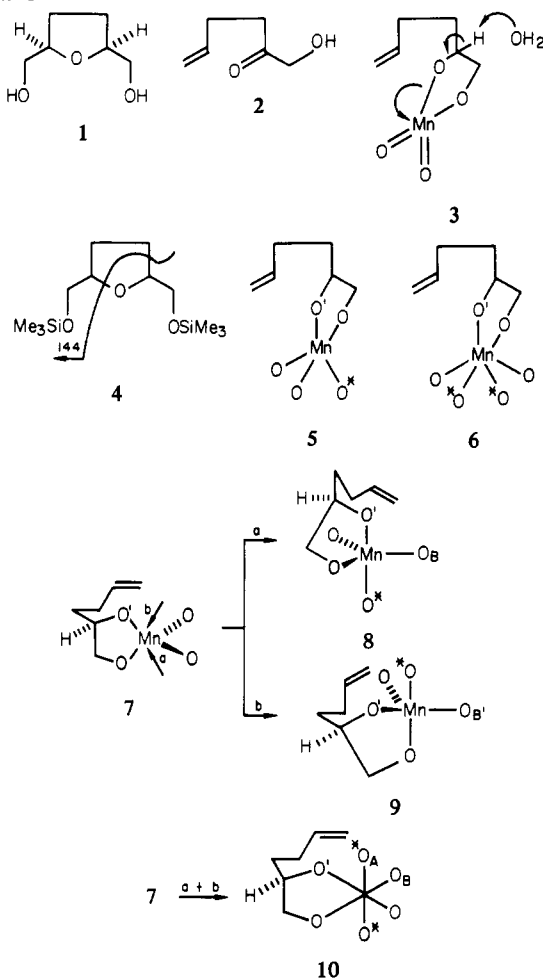
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(15) Baldwin, J. E.; Crossley, M. J.; Lehtonen, E.-M. *M. J. Chem. Soc., Chem. Commun.* **1979**, 918-920.

(16) This is the pH measured at the end of the reaction; pH control is maintained by passing a stream of carbon dioxide through the reaction mixture.

(17) Identified by direct comparison with authentic material, prepared by Mr. K. M. Oswald according to Malherbe and Dahn (Malherbe, R.; Dahn, H. *Helv. Chim. Acta* **1974**, *57*, 2492-2503).

Scheme I



that the incorporation is not quantitative. Analysis of the *m/e* 261 and 144 regions of these mass spectra revealed that one of the hydroxyl oxygens of the product carried the label and the incorporation of solvent at this position was 50%.

This finding is incompatible with the mechanism proposed by Klein and Rojahn⁴ and by Walba¹⁴ for the oxidation of 1,5-hexadiene, in which all three oxygen atoms of the product are derived from a single molecule of permanganate via a 1:1 diene-permanganate complex. The fact that a symmetrical substrate is converted into a symmetrical product in an unsymmetrical manner agrees with the suggestions of Sable^{9,23} and others¹⁵ that a sequential oxidation of the two double bonds occurs, via the manganate ester **3** (vide supra). However, the incorporation of solvent which is observed in the formation of **1** cannot involve a direct attack upon the terminal olefinic carbon atom of **3**, since this will lead to *cis* oxygenation of one double bond and *trans* oxygenation of the other. It must be concluded that the solvent is transferred to carbon via the manganese atom, i.e., that a pentacoordinated species (**5**²⁴) or a hexacoordinated species (**6**²⁵) transfers O' and one other oxygen to the second double bond.

However, the pH control during the oxidation is maintained with a stream of carbon dioxide which may undergo oxygen exchange with water,²⁶ and the acetone solvent may also undergo oxygen exchange with water. Therefore, the observed 50% incorporation might well represent a minimum value. Since the rates of oxygen exchange of carbon dioxide and acetone under the

present reaction conditions are unknown, it was decided to repeat the labeling experiments in the complementary sense, i.e., using ¹⁸O-labeled permanganate and unlabeled water.

Labeled samples of permanganate were prepared²⁷ by heating potassium permanganate at 90 °C for varying times in 92% or 97% enriched H₂¹⁸O, followed by evaporation of the solvent, and the relative proportions of the molecules containing 0, 1, 2, 3, and 4 atoms of ¹⁸O were determined by ⁵⁵Mn NMR.²⁸ This information allowed the mass spectrum of **4** prepared from a labeled permanganate sample to be calculated with the assumptions that two of the oxygen atoms or all three of the oxygen atoms are derived from the oxidizing agent.²⁹ Table I shows the result of a typical run, in which these calculated values are compared to those found experimentally. The experimental result is consistent with the conclusion that 2.5 atoms of oxygen of the anhydro tetrol are derived from the permanganate and 0.5 atom from the solvent.

Manganate is known to be tetrahedral.³⁰ Addition of one molecule of water to the chiral tetrahedral ester **7**, from a direction *trans* to a Mn–O bond, will lead to a 1:1 mixture of the penta-coordinate esters **8** and **9**.³¹ If it is assumed that these have a trigonal-bipyramidal geometry and an apical-equatorial fusion of the five-membered ring,³² then **8** can transfer O' and only the equatorial oxygen labeled O_B, derived from the permanganate, to the second double bond. However, **9** can transfer O' and either the apical oxygen labeled *O, derived from the solvent, or the equatorial oxygen labeled O_B, derived from the permanganate. Transfer from the apical position is expected to be preferred.³³ This analysis is consistent with the experimental results provided that oxygen scrambling and/or interconversion of **8** and **9** are not competitive with the second oxidation.

Alternatively, addition of two molecules of water to **7** will lead to the octahedral hexacoordinate ester **10**.³¹ In the enantiomer shown, *O_A, derived from the solvent, and O_B, derived from the permanganate, are diastereotopic, and only *O_A has the correct geometry for addition, together with O', to the second double bond. Oxidation of the second double bond by a hexacoordinate manganate ester would therefore lead to an anhydro tetrol in which two oxygens are derived from the permanganate and one from the solvent. This analysis is inconsistent with the experimental results unless oxygen scrambling is competitive with the second oxidation or the solvent molecules have a *cis* configuration in **10**.

Thus, the data appear to provide evidence for the intervention of a manganese complex with coordination number greater than four. However, the unprecedented nature of **8–10** and the lack of information concerning oxygen scrambling and/or interconversion of such species suggest that a decision concerning the precise nature of the intermediate should be deferred.

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(27) Wiberg, K. B.; Stewart, R. *J. Am. Chem. Soc.* **1955**, *77*, 1786–1795.

(28) The analysis takes advantage of an oxygen isotope effect on the ⁵⁵Mn chemical shift. See: Haase, A. R.; Lutz, O.; Müller, M.; Nolle, A. *Z. Naturforsch. A* **1976**, *31A* 1427–1428. Buckler, K. U.; Haase, A. R.; Lutz, O.; Müller, M.; Nolle, A. *Ibid.* **1977**, *32A*, 126–130. The spectra of the present work were obtained on a Bruker WM250 spectrometer.

(29) Assuming no oxygen isotope effect in the reaction, there are six ways in which two of four oxygens can be transferred to a substrate, and four ways in which three of four oxygens can be transferred.

(30) Wroblewski, J. T.; Long, G. T. *J. Chem. Educ.* **1977**, *54*, 75–79.

(31) The location of the hydroxyl protons is not specified in this structure.

(32) See, e.g.: Holmes, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 433–446.

(33) This follows from the general finding that bonds to apical ligands are longer and weaker than bonds to equatorial ligands. See, e.g.: Martin, J. C.; Perozzi, E. F. *Science (Washington, D.C.)* **1976**, *191*, 154–159.

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(24) See: Scharnow, B. Z. *Anorg. Allgem. Chem.* **1933**, *215*, 185–189.

(25) See: Criegee, R.; Marchand, B.; Wannowius, H. *Liebigs Ann. Chem.* **1942**, *550*, 99–133. Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263–4265. Schröder, M. *Chem. Rev.* **1980**, *80*, 187–213.

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