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Oxidation of Olefins by Potassium Permanganate. ^{18}O-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-glycol[1] 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 latter is the "normal" product of the permanganate oxidation of a terminal olefin under these reaction conditions.[2] Its formation indicates[2] 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).

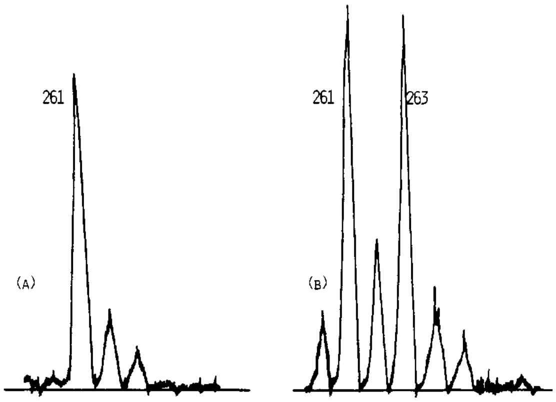

Figure 1. (A) *m/e* 261 region of the mass spectrum of **4**. (B) *m/e* 261 region of the mass spectrum of **4** prepared by oxidation of 1,5-hexadiene with potassium permanganate in a solvent containing 92% enriched $H_2{}^{18}O$. The data were obtained on a Finnigan 31000 GC/MS instrument, by using 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 ^{18}O-Labeled Potassium Permanganate[a]

m/e	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 ^{18}O are, respectively, 39.2, 35.7, 15.7, 6.9 and 2.2. [b] Average of six determinations. The error is ±1%.

The bis(trimethylsilyl) ether **4** exhibited an M + 1 peak at *m/e* 277 under CI-MS conditions and an M − 15 peak[18] 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 $H_2{}^{18}O$. 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,

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

(1) Wagner, G. *J. Russ. Phys. Chem. Soc.* **1895**, *27*, 219.

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

(3) Wiberg, K. B.; Saegebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 2822-2824.

(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 tetrols[6] 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.[8] 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 acid[11] are oxidized to 1,2-anhydro tetrols; levopimaric acid gives a 1,4-anhydro tetrol;[12] and occidentalol yields a 2,3-anhydro tetrol.[13] The oxidation of 1,5-dienes[4] leads to 2,5-anhydro tetrols, and these are formed by cis oxygenation of *both* double bonds.[14,15]

(6) Wagner, G. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2307-2018. Wallach, O. *Liebigs Ann. Chem.* **1909**, *368*, 1-22; **1908**, *362*, 285-304. Zelinskii, N. D.; Titowa, A. N. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 1399-1406. McCasland, G. E.; Furata, S.; Johnson, L. F.; Shoolery, J. N. *J. Org. Chem.* **1963**, *28*, 894-900.

(7) Lemieux, R. U.; Von Rudloff, E. *Can. J. Chem.* **1955**, *33*, 1710-1713.

(8) ApSimon, J. W.; Chau, A. S. Y.; Craig, W. G.; Krehm, H. *Can. J. Chem.* **1967**, *45*, 1440-1445: Personal communication from Professor J. W. ApSimon.

(9) Powell, K. A.; Hughes, A. L.; Katchian, H.; Jerauld, J. F.; Sable, H. Z. *Tetrahedron* **1972**, *28*, 2019-2027.

(10) Anastasia, M.; Fiecchi, A.; Scala, A. *J. Org. Chem.* **1979**, *44*, 3657-3661.

(11) Ruzicka, L.; Sternbach, L. *Helv. Chim. Acta* **1938**, *21*, 565-583; **1940**, *23*, 333-341, 341-345. The stereochemistry of the product was not established.

(12) Herz, W.; Ligon, R. C. *J. Org. Chem.* **1972**, *37*, 1400-1405.

(13) Von Rudloff, E. *Tetrahedron Lett.* **1966**, 993-998. The stereochemistry of the product was not determined.

(14) Walba, D. M.; Wand, M. D.; Wilkes, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4396-4397.

(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).

(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 media[20] and both oxyanions are in equilibrium with permanganate by a combination of oxidation[21] 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 adipoin[2] under Klein and Rojahn's conditions for the oxidation of **3**, in a mixture of acetone (90%) and 12.5% enriched $H_2{}^{18}O$ (10%), and the product was examined by mass spectrometry. No incorporation of ^{18}O was observed.

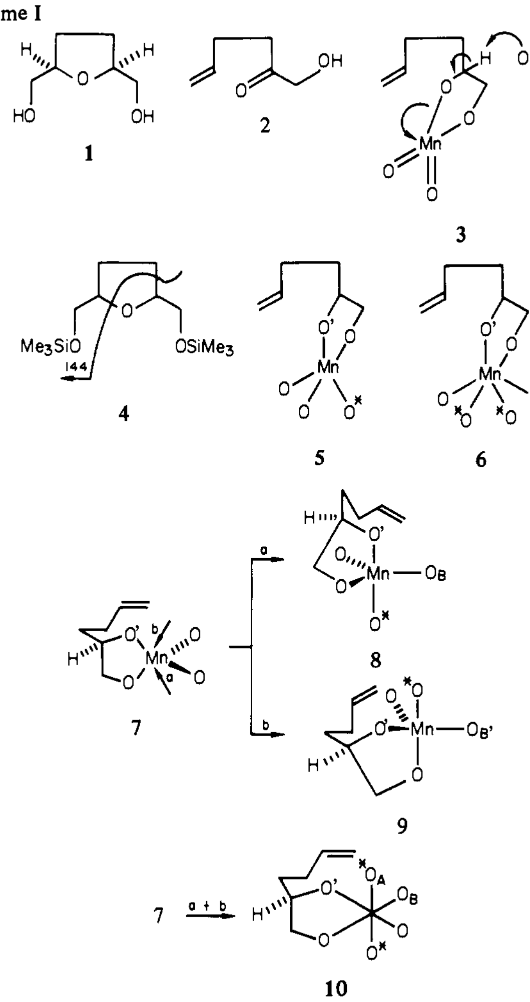
(20) Heckner, K.-H.; Landsberg, R. *J. Inorg. Nucl. Chem.* **1967**, *29*, 423-430.

(21) Lister, M. W.; Yoshino, Y. *Can. J. Chem.* **1960**, *38*, 2342-2348.

(22) Sheppard, J. C.; Wahl, A. C. *J. Am. Chem. Soc.* **1957**, *79*, 1020-1024.

0002-7863/81/1503-940$01.25/0

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 Rojahn[4] and by Walba[14] 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 others[15] 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 ^{18}O-labeled permanganate and unlabeled water.

Labeled samples of permanganate were prepared[27] by heating potassium permanganate at 90 °C for varying times in 92% or 97% enriched $H_2{}^{18}O$, followed by evaporation of the solvent, and the relative proportions of the molecules containing 0, 1, 2, 3, and 4 atoms of ^{18}O were determined by ^{55}Mn 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 pentacoordinate 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 manganese 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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(23) Sable, H. Z.; Powell, K. A.; Katchian, H.; Niewoehner, C. B.; Kadlec, S. B. *Tetrahedron* **1970**, *26*, 1509–1524.

(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.

(26) Kern, D. M. *J. Chem. Educ.* **1960**, *37*, 14–23.

(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 ^{55}Mn 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) Wrobleski, J. T.; Long, G. T. *J. Chem. Educ.* **1977**, *54*, 75–79.

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

(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.