

icates that the A and B conformations of 1,3-dioxepane are 1-1.6 kcal mol⁻¹ less stable than the D conformation rather than the ~2.6 kcal mol⁻¹ previously calculated.¹

Evaluation of the energies of the boat and twist-boat conformations of **2a** and **3a**, making the same assumptions as previously, indicated that for both **2a** and **3a** there are two enantiomeric TB conformations which are considerably more stable than any others of this type and also similar in energy to the most stable TC conformations. However, neither the ¹³C NMR evidence nor the equilibrium results are compatible with a significant proportion of TB conformations.²¹ We therefore conclude that the TB conformations of 1,3-dioxepane are considerably less stable than calculated, perhaps by as much as 2 kcal mol⁻¹.

Thus, the examination of the conformational properties of 2,4,7-trisubstituted-1,3-dioxepanes gave considerable information about the conformational properties of 1,3-dioxepane.

The scheme outlined here can provide conformational information about any seven-membered ring. For instance, examination of the pseudorotational itineraries in Figure 1 shows that equilibrium of the same stereoisomers of cycloheptane would yield the axial-equatorial energy difference.

Acknowledgment. T.B.G. is grateful to the NSERC of Canada for support. We thank Dr. Charles Rodgers of Bruker Canada for the 250-MHz NMR spectra.

(21) Variable-temperature 250-MHz ¹H NMR spectra of **3b-d**, compounds in the series (**3**) most likely to exist in TB or B conformations, down to 118 K showed that pseudorotation had slowed (ΔG^\ddagger 6.4-7.0 kcal mol⁻¹ from coalescence measurements) but gave no indication of the presence of other than TC conformations.

Oxidation of Olefins by Potassium Permanganate. Mechanism of α -Ketol Formation

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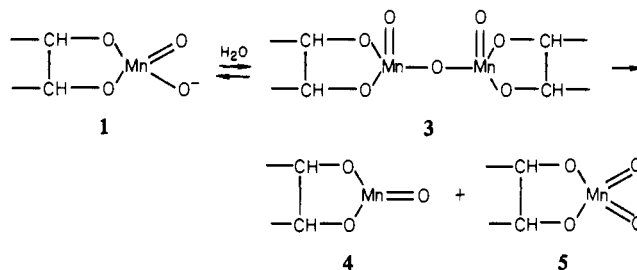
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Received September 2, 1980

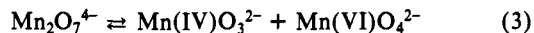
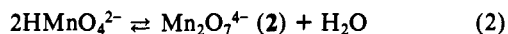
The oxidation of an olefin by potassium permanganate in aqueous media can lead, inter alia, to an α -glycol,¹ a 2-equiv oxidation, or α -ketol,² a 4-equiv oxidation. The glycol is a major product at pH >9 (cyclic olefins)³ or pH >12 (acyclic olefins);¹ the ketol is a major product in the pH range 4-8^{2,4} and is not formed via the glycol.⁵ At pH values intermediate between the optimum for glycol formation and the optimum for ketol formation, both products are observed, and the ketol/glycol ratio can be increased by an increase in the initial permanganate/olefin ratio.^{5b} With the periodate-permanganate reagent,⁶ oleic acid

is oxidized exclusively to ketol, even at pH 12.^{5b} These various observations suggest that the glycol and the ketol arise from a common intermediate, which may react with hydroxyl ions to form the lower oxidation level product or with hydroxyl ions and permanganate (or periodate) to form the higher oxidation level product.

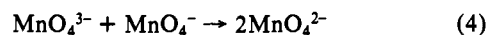
The cyclic hypomanganate ester **1**⁷ is considered to be an intermediate in the formation of the glycol and to undergo hydrolysis with fission of the Mn-O bonds, on the basis of the stereochemistry of the reaction,⁸ ¹⁸O-labeling experiments,⁹ and kinetic studies.^{10,11} The kinetic results support the view that the glycol and the ketol are formed from a common intermediate, since the second-order rate constant is the same at pH 6.8 and 13.¹⁰ It follows, therefore, that the ketol arises by oxidative hydrolysis of the cyclic ester **1**.



The oxidative and hydrolytic reactions of inorganic hypomanganate (MnO₄³⁻) with permanganate, periodate, and water have been studied in some detail.¹² The reaction with water (eq 1-3) leads to disproportionation^{12a,b} and oxygen exchange^{12c} via



the dimeric species **2**. Extrapolation to pH 7 of the data of ref 12b indicates that, at 25 °C, the observed second-order rate constant for disproportionation will be greater than 10¹² M⁻¹ s⁻¹. This is much larger than the rate constants for the oxidation of hypomanganate by permanganate (eq 4) and periodate (eq 5) (2.8



× 10⁶ M⁻¹ min⁻¹ and 20 × 10⁶ M⁻¹ min⁻¹, respectively, at 35 °C).^{12d} An analogous protonation and dimerization of the ester **1** leads to **3** which, upon electron transfer (cf. eq 3), disproportionates to the Mn(IV) ester **4** and the Mn(VI) ester **5**. A species corresponding to **4** has apparently been observed by several groups of workers¹³ and found to undergo oxidation to **5** in the presence of excess permanganate.^{13b} These considerations suggest that, in neutral media, the Mn(V) ester **1** is transformed rapidly into the Mn(VI) ester **5**.

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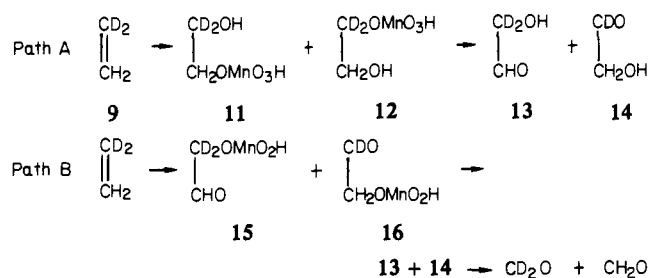
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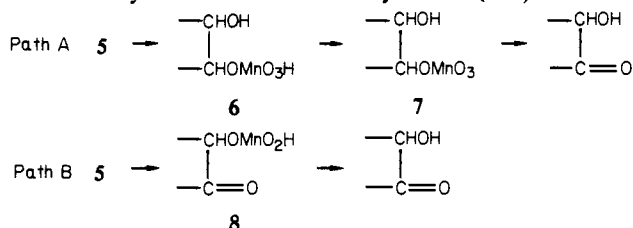
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Scheme I



The conversion of **5** to α -ketol can proceed via one of two paths. Path A involves hydrolysis of the ester to the acyclic Mn(VI) ester **6** which may be oxidized to the acyclic Mn(VII) ester **7**.¹⁴



Oxidative decomposition of **6** (or **7**) would then lead to ketol. Alternatively, path B supposes oxidative decomposition of **5** to **8**, the Mn(IV) ester of the ketol, which is hydrolyzed to the product. The two mechanisms differ in the timing of the oxidative and hydrolytic steps and are, in principle, distinguishable by deuterium labeling experiments. However, such experiments must be applied to the product-determining step of the reaction, because the rate-determining step (formation of **1**)¹⁰ does not involve C-H bond breaking.¹⁵

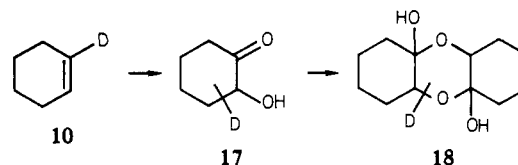
The required information was secured by an examination of the ketol-forming oxidations of the symmetrical olefins ethylene-1,1-*d*₂ (**9**)¹⁶ and cyclohexene-1-*d* (**10**).¹⁷ As outlined in Scheme I, oxidation of **9** via path A should lead to an approximately 1:1 mixture of acyclic esters **11** and **12**, since no significant isotope effect is expected in the hydrolysis step. The mixture of **11** and **12** will be transformed to an approximately 1:1 mixture of the two glycolic aldehydes **13** and **14**. On the other hand, in the first step of path B, oxidative decomposition may proceed with either C-H bond breaking, to form **15**, or C-D bond breaking, to form **16**. An isotope effect is expected in this step, leading to an excess of **15** over **16**. The mixture of **15** and **16** will be transformed to a mixture of **13** and **14**, in which the former compound predominates. Application of the same argument to the substrate **10** leads to the prediction of 50% retention of deuterium in the product in the case of path A and greater than 50% retention of deuterium in the case of path B. The two mechanisms are therefore distinguishable, unless **11** and **12** interconvert rapidly prior to oxidative decomposition. However, this seems unlikely in view of the nature of the reactions involved.

Oxidation of ethylene to glycolic aldehyde was found to occur with the periodate-permanganate reagent. Optimum conversion to this product was achieved in a system containing periodate (2

mmol), permanganate (0.2 mmol), potassium carbonate (2 mmol), and water (40 mL), stirred rapidly in an ethylene atmosphere. Extensive control experiments revealed that the initial rapid oxidation of the olefin led to a mixture of ethylene glycol (19%), glycolic aldehyde (71%), and glyoxal (10%), that the slower periodate oxidation of glycolic aldehyde was more rapid than that of ethylene glycol and could be made selective with short reaction times, and that the formaldehyde product of this secondary oxidation could be precipitated quantitatively as its 2,4-dinitrophenylhydrazone, after quenching of the reaction. Analysis of the IR spectra of the dinitrophenylhydrazones of formaldehyde and formaldehyde-*d*₂¹⁶ revealed absorption at 728 and 720 cm⁻¹, respectively, which could be used to determine the composition of mixtures to an accuracy of $\pm 2\%$.

After 10 min, 1 h, 6 h, and 24 h, the oxidation of **9** by periodate-permanganate, as described above, led to formaldehyde 2,4-dinitrophenylhydrazone containing 68%, 58%, 58%, and 58% of formaldehyde-*d*₂, respectively. These results are consistent with path B. The percentage of deuterium in the product decreases with increasing reaction time because of the contribution to the total formaldehyde pool from the slower oxidation of ethylene-1,1-*d*₂ glycol, also present in the reaction mixture. The fact that the deuterium content becomes constant after 1 h indicates that exchange with the solvent is not important under the reaction conditions. As a further check on the validity of the reaction system and the analytical procedures, **9** was oxidized by periodate-osmium tetroxide;¹⁸ the consumption of oxidant (4 equiv/mol of olefin) and the yield of formaldehyde (2 equiv/mol of olefin) were those expected for quantitative conversion of olefin to ethylene glycol, and the IR spectrum of the dinitrophenylhydrazone indicated a 1:1 mixture of formaldehyde and formaldehyde-*d*₂.

In aqueous ethanol or acetone at pH > 8, permanganate oxidation of cyclohexene led only to glycol and adipic acid. With an excess of sodium bicarbonate in the reaction mixture, traces of the ketol, adipoin, were detected. However, in aqueous acetone at -10 °C and in the presence of a stream of carbon dioxide, the yield of glycol was reduced to <1%, and adipoin (**17**), isolated as the dimer **18**,¹⁹ was formed in 20-30% yields. The dimer,



which is in equilibrium with **17** in aqueous solution,²⁰ was recovered unchanged following exposure to a stream of carbon dioxide in D₂O-acetone at -10 °C. The glycol was also recovered unchanged following exposure to permanganate under the conditions of ketol formation. Under both electron impact and chemical ionization conditions, the mass spectrum²¹ of **18** appeared as that of **17**. The oxidation of **10** (88.5% *d*₁) then afforded **18-d**, which was found to have retained 73% of its deuterium (average of CI-MS and EI-MS measurements).

The present results involving the conversion of **10** to **18** confirm the conclusions reached in 1957^{3b} that the permanganate or periodate-permanganate oxidation of an olefin to ketol in aqueous media proceeds by oxidative decomposition of a cyclic manganese ester, followed by hydrolysis of the resulting Mn(IV) ester.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

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(15) An alternative mechanism for ketol formation, which does not involve oxidative decomposition of manganese esters, can also be proposed. If it is assumed^{12a} that hypomanganate can oxidize water, i.e., $\text{MnO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{HMnO}_4^{3-} + \text{OH}$, the oxidation of a glycol might then be performed by the resulting hydroxyl radicals (see, e.g.: Waters, W. A. *Nature (London)* **1946**, *158*, 380. Baxendale, J. H.; Evans, M. G.; Park, G. S. *Trans. Faraday Soc.* **1946**, *42*, 155-169). To check this possibility, oleic acid was oxidized to ketol by permanganate in the presence of varying amounts of the derived glycol, erythro-9,10-dihydroxystearic acid. The glycol was recovered unchanged, and the yield of the olefin \rightarrow ketol oxidation was unaffected.

(16) This compound was generously provided by Dr. L. C. Leitch, NRCC, Ottawa.

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(20) An aqueous solution of the dimer **18** contains 10% of the monomer **17** (Shurvell, H. F., unpublished results).

(21) Obtained at 70 eV on a Du Pont 21-491B spectrometer by Mr. P. R. Gordon, Du Pont Research Centre, Kingston, whose assistance is gratefully acknowledged.