Tetralkylammonium Permanganate Epoxidation of an Unreactive Double Bond by an Intramolecular Oxygen-atom Transfer Process

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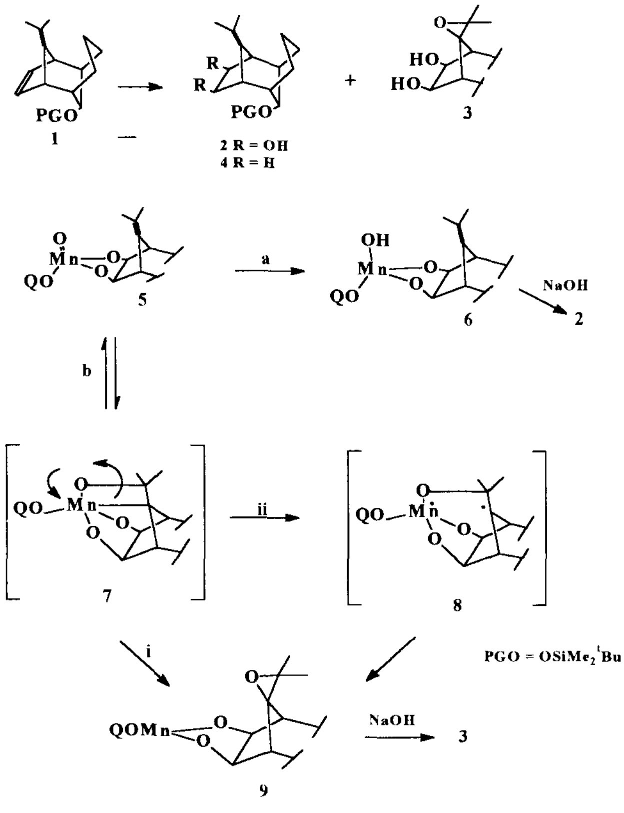
(Received September 22, 1997; CL-970736)

The ammonium permanganate oxidation of a tricyclic, rigid diene gives the mono- dihydroxylated compound together with the diol- epoxide derivative. The epoxidation involves an intramolecular oxygen- atom transfer process from the anchored manganese (V) diester to the second double bond.

As a part of a project directed to the synthesis of new synthetic receptors for the recognition of nucleic bases we needed to transform diene **1** into diol **2** for further synthetic manipulations of the system. Because of the extremely low chemical reactivity of the exocyclic double bond[1] we planned to achieve this transformation by regioselective syn-dihydroxylation at the most reactive centre.[2] Treatment of **1** with one equivalent of triethylbenzylammonium permanganate[2b] at -50°C and quenching with 3% aqueous sodium hydroxide afforded a mixture of two compounds: the expected diol **2** (70%) and a minor compound identified as the diol epoxide **3** (20%).[3] Higher temperatures gave a poorer diol yield and varying amounts of **3** together with the dialdehyde derivative.[2b] Stoichiometric OsO_4[2a] gave the required diol **2** in 88% yield. $VO(acac)_2/{}^tBuOOH$ epoxidation of **2** gave the diol epoxide **3** in 82% yield, presumably through a vanadate ester transition state[4] in which the metal is coordinated to both hydroxy groups of the diol.

The unexpected formation of **3** in this reaction can be rationalised by the mechanism depicted in Scheme 1. The cyclic manganese(V) diester **5**, formed by attack of the permanganate on the most reactive double bond, decomposes into diol **2** or epoxy-diol **3** through two different reduction processes: one-electron reduction by reaction with the solvent to give the manganese (IV) diester **6**[5] (path a) or an intramolecular oxygen transfer to the other double bond which lies in close proximity to the manganese centre (path b). The intramolecular nature of this epoxidation is confirmed by the following features: i) the limiting amount of oxidant, -one equivalent of permanganate-, and the quantitative conversion of diene into dihydroxylated products excluding the participation of more than one mole of permanganate per mole of diene in the overall process; ii) alkene **4** is not epoxidised by ammonium permanganate (2 eq., r.t., overnight), and iii) diol **2** does not react with ammonium permanganate within of the temperature range used to oxidise diene **1** (1 eq., -78°C, 1h; -78 to -30°C, 1h; r.t., 1h)

The way by which the oxygen atom is transferred is unknown but it is likely to proceed following a similar mechanism to that involved in the epoxidation of alkenes catalysed by oxo-manganese (V) porphyrins or cationic oxo-manganese (V) Salem complexes.[6] CPK models and molecular minimisation of the intermediate **5** reveal that the tetrahedral manganese (V) centre places the metal oxo double bond nearly parallel to the isopropylidene group making unlikely an orthogonal approach of both centres to form a charge-transfer complex or to produce a concerted "oxene" insertion.[6] On the other hand, the parallel orientation of both oxo - metal double bond and alkene favours the reversible formation of a highly strained metallooxetane intermediate **7**,[7] which irreversibly rearranges to the epoxide following two possible different routes: i) direct carbon migration from manganese to oxygen atom, or ii) homolytic cleavage of the manganese- carbon bond to give the stabilised radical intermediate **8** which collapses to the epoxide. Basic hydrolysis of the epoxide- manganese (III) diester **9** affords the epoxide- diol **3**. The absence of rearrangement compounds supports the idea of a direct rearrangement but the other possibility cannot be excluded.



Scheme 1.

To the best of our knowledge this is the first case in which potassium permanganate reacts with a diene to produce an epoxy-diol in non-aqueous media.[8,9]

This work was supported by the Spanish Ministerio de Educación y Ciencia, DGICYT grants PB94-0028 and PB91-0149. JRC thanks the ICI for a predoctoral grant.

References and Notes

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8 Aqueous potassium permanganate oxidizes 1,3-dienes into all-cis anhydrotetrols and 2,5-dienes into 2,5-anhydrotetrols with the incorporation of one oxygen atom from the solvent. A manganese (VI) diester has been postulated such as the active intermediate which intramoleculary reacts with the neighbouring double bond to afford the epoxy-diols. See: A. J. Fatiadi, *Synthesis*, **1987**, **85** and references cited therein.

9 One of the referees points to the possibility of a hydroxy- assisted epoxidation by permanganate. The inertia of diol **2** to be epoxidated by ammonium permanganate under the same reaction conditions as diene **1** rules out such a possibility.