

The Key Role of Water in the Heterogeneous Permanganate Oxidation of ω -Hydroxy Alkenes

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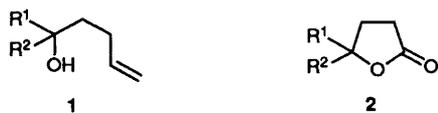
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Potassium permanganate–copper sulphate in dichloromethane in the presence of a catalytic amount of water effects a smooth oxidative cyclization of ω -hydroxy alkenes to ω -lactones in good yields with the net loss of one or more carbon atoms in the process.

The rate of heterogeneous reactions catalysed by phase transfer agents has been shown to be enhanced by the addition of catalytic amounts of water.¹ Recently, a non-classical phase transfer system, *i.e.* Ω phase, has been invoked to explain the role of water in these reactions.² More recently, we have reported³ the Ω -phase catalysis in the direct oxidation of alkenes to α -diketones or α -hydroxy ketones with a mixture of potassium permanganate and copper sulphate in the presence of a catalytic amount of *t*-butyl alcohol and water. It is believed that in this case the alcohol acts as a phase transfer

catalyst and together with the water forms the third phase over the surface of the inorganic solid in which the reaction takes place. In this communication, we report our results on a facile oxidative cyclization of ω -hydroxy alkenes to ω -lactones with potassium permanganate under Ω -phase catalysis.[†]

Although potassium permanganate–copper sulphate⁴ is inert to ω -hydroxy alkenes in dichloromethane at 28 °C even after 24 h, with the addition of a catalytic amount of water, an exothermic reaction ensues resulting in the formation of

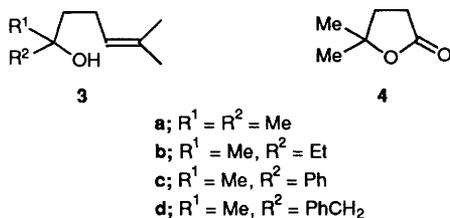


- a;** $R^1 = R^2 = H$
b; $R^1 R^2 = -[CH_2]_4-$
c; $R^1 R^2 = -[CH_2]_5-$
d; $R^1 = R^2 = Me$
e; $R^1 = H, R^2 = Et$

[†] Oxidation of compound **3c**: A mixture of solid $KMnO_4$ (8 g) and $CuSO_4 \cdot 5H_2O$ (4 g) was ground to a fine powder. Water (400 μ l) was added, and to a stirred suspension of this slightly wet mixture in dichloromethane (20 ml) was added the hydroxy alkene **3c** (2 mmol) in dichloromethane (5 ml). The reaction mixture started to reflux for ≈ 5 min and then cooled. The mixture was then stirred for 3 h at room temperature (28 °C), filtered through Celite and washed with dichloromethane. The solvent was removed to afford the lactone **4c**⁵ (81%) as a colourless oil, after chromatography purification on silica gel (eluant, 1:5 ethyl acetate–light petroleum); ν_{max}/cm^{-1} (neat) 3080, 3060, 1775 and 1600; 1H NMR ($CDCl_3$) δ 1.72 (s, 3 H), 2.35–2.69 (m, 4 H) and 7.3 (s, 5 H); m/z 176 (M^+).

Table 1 KMnO₄-CuSO₄ oxidation of ω-hydroxy alkenes

Substrate	t/h	Product ^a	Yield (%)
1a	6	2a	52
1b	4.5	2b	64
1c	4	2c	71
1d	4.5	2d	78
1e	4	2e + 9 (1:2)	84
3a	4	4a	76
3b	4	4b	72
3c	3	4c	81
3d	3.5	4d	78
5	12	6	56
7a	7	8a	63
7b	4.5	8b	69
10	4.5	11	53

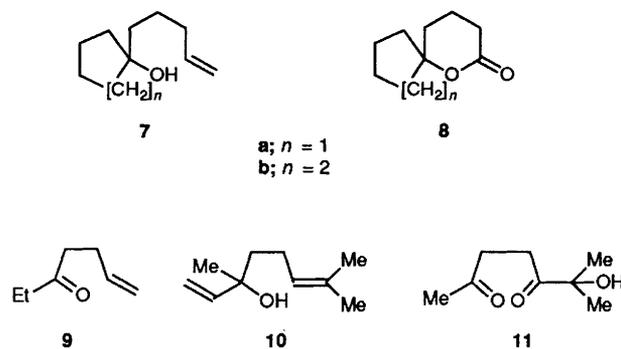
^a All products gave satisfactory spectra and elemental analyses.^b Isolated yields.

ω-lactones⁵ in good yields with a net loss of one or more carbon atoms in the process.‡ The results on the facile oxidative cyclization of a wide variety of ω-hydroxy alkenes to ω-lactones under Ω-phase catalysis§ are summarized in the Table 1.¶ Compound **1a** containing a primary hydroxy group underwent a smooth oxidative cyclization to yield lactone **2a** without forming any other product resulting from oxidation of the hydroxy group. However, compound **1e** containing a secondary hydroxy group gave a mixture of lactone **2e** and the ketone **9** (1:2). Linalool **10** containing an allylic hydroxy group suffered oxidative cleavage and oxidation of the trisubstituted alkenic moiety to produce the keto-alcohol **11**.³

‡ In the absence of CuSO₄·5H₂O, solid KMnO₄ alone does not effect this transformation.

§ The reaction takes place in the absence of t-butyl alcohol and phase transfer catalysts.

¶ *Spectral data for 6:* ν_{max}/cm⁻¹ (neat) 1775; ¹H NMR (CDCl₃) δ 1.39 (s, 3 H) and 1.3–2.7 (m, 11 H); *m/z* 154 (M⁺). **4d:** ν_{max}/cm⁻¹ (neat) 3080, 3060, 1770 and 1600; ¹H NMR (CDCl₃) δ 1.44 (s, 3 H), 1.91–2.15 (m, 2 H), 2.16–2.27 (m, 1 H), 2.35–2.5 (m, 1 H), 2.94 (d, 2 H, *J* = 3.75 Hz) and 7.21–7.35 (m, 5 H); *m/z* 190 (M⁺). **11:** ν_{max}/cm⁻¹ (neat) 3450, 1720 and 1705; ¹H NMR (CDCl₃) δ 1.43 (s, 6H), 2.2 (s, 3 H), 2.83 (s, 4 H) and 3.76 (br s, 1 H); *m/z* 159 (M⁺ + 1).



We believe that this reaction is a substituted (hydroxy) directed oxidation and the addition of a small amount of water to a heterogeneous solid-liquid medium has the same effect as crown ethers and other phase transfer agents. The reaction probably takes place at the water-coated surface of solid KMnO₄-CuSO₄, *i.e.* Ω-phase.¶ The key role of water in the Wittig-Horner reaction in heterogeneous solid-liquid systems has recently been demonstrated by Delmas.⁶

Thus the present methodology illustrates an effective utilization of the classical permanganate ion in effecting a useful and important synthetic transformation under very mild reaction conditions and compares favourably with other methods⁷ for effecting such a transformation.

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¶ Similar to the observations of Liotta,² in our experiments we find that there is an appreciable decrease in the concentration of the substrate **1** in the organic phase, 10 min after the addition of water. Ω-phase formation has been found to occur with triglyme and tetraglyme in the presence of catalytic amounts of water.²