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Regioselective hydroxylactonization of γ,δ-unsaturated carboxylic acids with hydrogen peroxide catalyzed by methyltrioxorhenium

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Abstract

The oxidation of unsaturated carboxylic acids and esters to lactones with hydrogen peroxide is catalyzed by methyltrioxorhenium (MTO). The reaction proceeds regioselectively in high yield. On the basis of the results of this investigation and a comparison with previous work, a concerted process and mechanism have been suggested.

Keywords: Catalysis; Rhenium; Peroxide; Lactonization

1. Introduction

Functionalized γ-lactones serve as chiral building blocks in natural products synthesis [1] and as precursors to HIV-1 protease inhibitors [2,3]. Many are bioactive natural products [4,5]. Heteroatom cyclizations lead to γ-lactones; in certain cases this allows two neighboring chiral centers to be introduced selectively and concurrently [6]. Cyclizations of hydroxy acids and esters have been more widely studied, but with unsatisfactory yields [7]. Both β,γ- and γ,δ-unsaturated esters can be oxidized to hydroxy-γ-lactones by the asymmetric dihydroxylation [1].

γ-Lactones have been prepared from unsaturated carboxylic acids with iron porphyrins and iodosylbenzene [6]. Thallium salts induce the lactonization of unsaturated carboxylic acids in ca. 50% yield [8]. *m*-Chloroperbenzoic acid also lactonizes unsaturated carboxylic acids when used with a catalytic amount of Amberlyst-15 ion-exchange resin [9].

We report here a new result: treatment of γ,δ-unsaturated carboxylic acids and esters with H_2O_2 affords δ-hydroxy-γ-lactones in a single, high-yield step at room temperature when methyltrioxorhenium (MTO) is used as a catalyst.

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2. Results and discussion

A convenient and efficient method with H_2O_2 can be used to prepare γ-lactones from the γ,δ-unsaturated carboxylic acids and esters with MTO as the catalyst in chloroform. This method achieves nearly complete regioselectivity with more than 95% yield under mild conditions. The net reaction for the parent 4-pentenoic acid is given by:

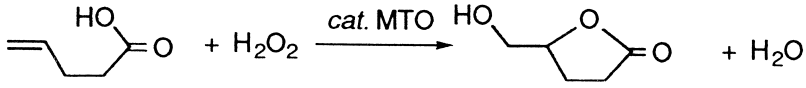


Table 1
Products of the MTO-catalyzed lactonization reactions

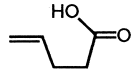
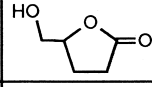
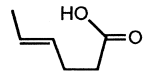
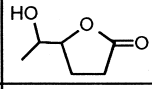
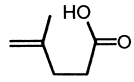
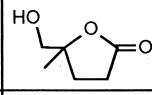
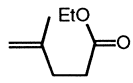
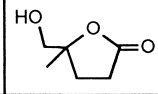
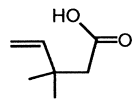
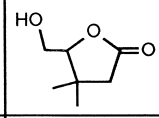
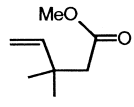
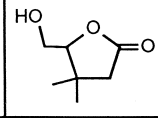
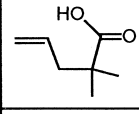
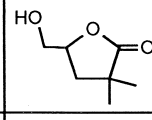
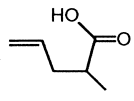
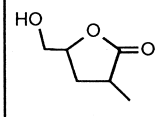
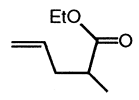
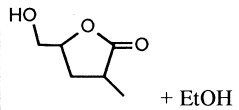
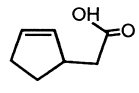
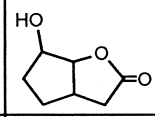
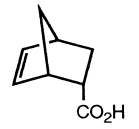
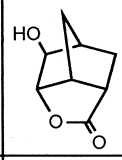
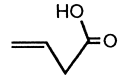
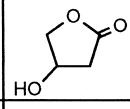
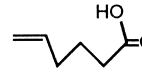
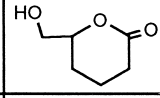
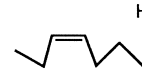
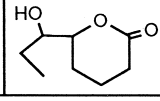
Entry	Reactant	Product (isomer ratio)	Yields (%)	Reaction time (hours)
1			98	14
2			97	9
3			98	9
4		 + EtOH	98	11
5			95	10
6		 + MeOH	95	14
7			98	10
8		 (0.89 : 1.0)	97	10

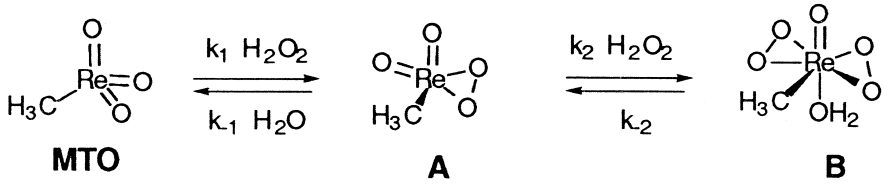
Table 1 (continued)

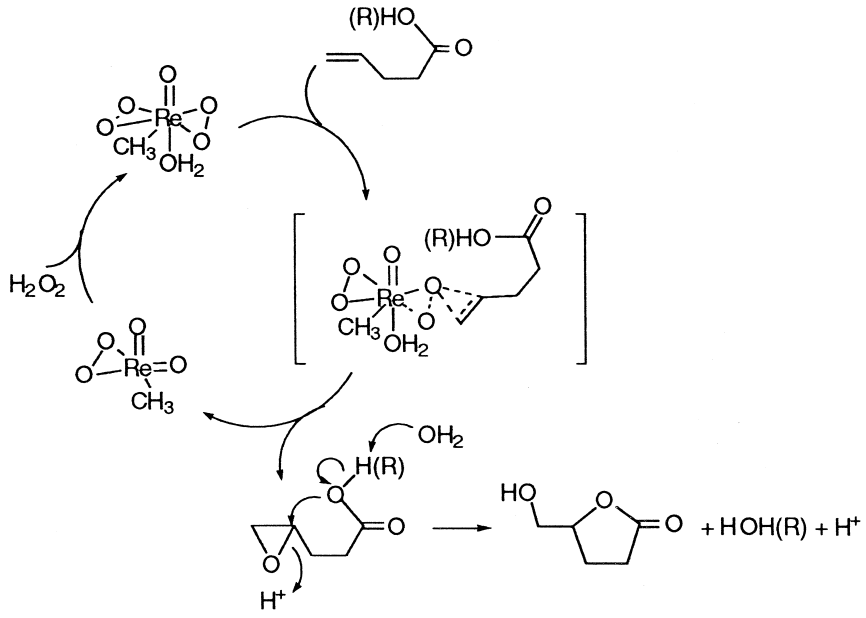
9		 + EtOH (0.89 : 1.0)	97	12
10			95	12
11			93	9
12 [a]			90	8
13 [b]			80 [c]	10
14			95	9

[a] The reaction temperature is 40°C.
[b] Solvent: $CDCl_3/CD_3CN = 1/1$
[c] The balance is 5,6-dihydroxyhexanoic acid.

Entries 1–3, 5, 7, and 8 in Table 1 illustrate the same reaction for unsaturated carboxylic acids with methyl substituents. Entries 4, 6 and 9 show the products obtained from esters that gave the same lactone products as the acids did. In the first seven entries only a single geometric isomer of the product is possible; the reactions went to 100% conversion with more than 95% selectivity.

As to the mechanism followed, we note that MTO is a well-established catalyst for reactions of hydrogen peroxide [10–12] including the epoxidation of alkenes [13–17] and the oxidative cyclization of hydroxyalkenes [18]. The active forms of MTO are the monoperoxo and diperoxo complexes formed in reversible equilibria:





Scheme 1.

The lactonized products may be formed via the epoxides of the unsaturated carboxylic acids (Scheme 1). The acidic protons that initiate the lactonization of epoxide could come from either the decomposition of MTO or the unsaturated carboxylic acid. The kinetic results did not show any difference between this reaction and the epoxidation reactions that we studied before [13–15]. The hydroxylactonization of the ester was only a little slower than that of the acid. To determine the reaction mechanism of the ester, urea hydrogen peroxide (solid) was used in acetonitrile instead of 30% aqueous hydrogen peroxide [15]. The product of Entry 6 was then the epoxide with ca. 100% yield in 14 h. Then 0.2 M $HClO_4$ was added to convert epoxide to lactone. This implicates the diol as a possible intermediate for ester hydroxylactonization. The small amount of acid needed for the homogeneous process very likely comes from the decomposition of MTO to perrhenic acid, a strong acid [19]. So MTO acts as a bifunctional catalyst in this reaction.

The products of Entry 8 were obtained as a mixture of stereoisomers (approximately 0.9:1.0), as determined from the ^{1}H-NMR spectra, showing an absence of stereochemical control in the reaction. However, these reactions proved to be highly regioselective in that a six-membered ring product was not obtained for lactones 1–11. These substrates all undergo an exo-5-tet cyclization [20]. The very slow cyclization of Entry 12 occurs by an endo-5-tet process. After one day, only 30% of the reactant had changed to product. At 40°C the lactonization reaction was complete in 8 h with a 90% yield.

Entries 13 and 14 were oxidized to tetrahydropyran-2-one. The reaction of 13 was too slow in chloroform, and after two days the product was a mixture of reactant and several products. To increase the solubility of MTO–H_2O_2, the binary solvent $CHCl_3$:CH_3CN (1:1) was used. After 9 h, 6-hydroxymethyl-tetrahydropyran-2-one and 5,6-dihydroxyhexanoic acid were obtained in a 4:1 ratio.

3. Experimental section

The general procedure used for these catalytic transformations was as follows: MTO (20 μmol) and H_2O_2 (0.50 mmol) in 1.0 ml chloroform was treated with the γ,δ-unsaturated carboxylic acid

Table 2
Data for the identification of furan and pyran reaction products; NMR (in $CDCl_3$) and MS data

5-hydroxymethyl-dihydro-furan-2-one **(1)**: ^{1}H NMR(/ppm): 4.61–4.68(m, 1H), 3.88–3.93(dd, $J = 12.6$, 2.7 Hz, 1H), 3.62–3.68(dd, $J = 12.6$, 4.8 Hz, 1H), 2.05–2.70(m, 4H); ^{13}C NMR(/ppm): 177.94, 80.92, 64.07, 28.72, 23.15; MS(EI): 177($M^+ + 1$), 99, 85.
5-(1-hydroxy-ethyl)-dihydro-furan-2-one **(2)**: ^{1}H NMR(/ppm): 4.40–4.43(m, 1H), 4.10–4.13(m, 1H), 2.53–2.61(m, 2H), 2.16–2.27(m, 2H), 1.18–1.20(d, $J = 5.1$ Hz, 3H); ^{13}C NMR(/ppm): 177.98, 83.74, 67.28, 28.68, 20.93, 17.74; MS(EI): 131($M^+ + 1$), 113, 85.
5-hydroxymethyl-5-methyl-dihydro-furan-2-one **(3)**: ^{1}H NMR(/ppm): 3.69–3.49(AB, $J = 12$ Hz, 2H), 2.61–2.85(m, 2H), 2.33–2.42(m, 1H), 1.91–1.99(m, 1H), 1.38(s, 3H); ^{13}C NMR(/ppm): 177.93, 87.04, 68.27, 29.72, 29.59, 23.07; MS(EI): 130(M^+), 113, 99.
5-hydroxymethyl-4,4-dimethyl-dihydro-furan-2-one **(5)**: ^{1}H NMR(/ppm): 4.17–4.19(m, 1H), 3.80–3.82(m, 2H), 2.32–2.53(m, 2H), 1.22(s, 3H), 1.13(s, 3H); ^{13}C NMR(/ppm): 177.11, 88.90, 61.35, 44.18, 38.20, 27.17, 21.64; MS(EI): 144(M^+), 127, 113.
5-hydroxymethyl-3,3-dimethyl-dihydro-furan-2-one **(7)**: ^{1}H NMR(/ppm): 4.56–4.59(m, 1H), 3.87–3.91(dd, $J = 12.8$, 3.2 Hz, 1H), 3.60–3.64(dd, $J = 12.8$, 5.2 Hz, 1H), 1.97–2.08(m, 2H), 1.29(s, 6H); ^{13}C NMR(/ppm): 182.47, 77.43, 63.65, 40.40, 37.94, 24.83, 24.79; MS(EI): 145($M^+ + 1$), 127, 113.
5-hydroxymethyl-3-methyl-dihydro-furan-2-one **(8)**: Cis: ^{1}H NMR(/ppm): 4.49–4.53(m, 1H), 3.89–3.93(m, 1H), 3.64–3.68(m, 1H), 2.72–2.80(m, 1H), 2.33–2.38(m, 1H), 1.73–1.85(m, 1H), 1.29(d, $J = 7.2$ Hz, 3H); ^{13}C NMR(/ppm): 179.95, 78.58, 64.31, 34.46, 31.64, 16.23; MS(EI): 131($M^+ + 1$), 113, 99. Trans: ^{1}H NMR(/ppm): 4.59–4.63(m, 1H), 3.84–3.89(m, 1H), 3.60–3.65(m, 1H), 2.80–2.87(m, 1H), 2.38–2.42(m, 1H), 1.95–2.02(m, 1H), 1.27(d, $J = 7.2$ Hz, 3H); ^{13}C NMR(/ppm): 180.99, 78.92, 63.53, 35.53, 31.64, 15.12; MS(EI): 131($M^+ + 1$), 113, 99.
2,3-dihydroxy-cyclopentaneacetic acid-γ-lactone **(10)**: ^{1}H NMR(/ppm): 4.73–4.75(d, $J = 6.9$ Hz, 1H), 4.34–4.36(m, 1H), 3.02–3.09(m, 1H), 2.79–2.88(m, 1H), 2.27–2.32(d, $J = 13.5$ Hz, 1H), 2.17–2.26(m, 1H), 1.84–1.91(m, 1H), 1.74–1.78(m, 1H), 1.50–1.57(m, 1H); ^{13}C NMR(/ppm): 177.86, 90.39, 76.28, 36.19, 35.67, 31.55, 30.80; MS(EI): 143(M^+-1), 125, 84.
5,6-dihydroxybicyclo[2.2.1]-octane-2-carboxylic acid-γ-lactone **(11)**: ^{1}H NMR(/ppm): 4.43–4.45(d, $J = 5.1$ Hz, 1H), 3.73(s, 1H), 3.15–3.19(m, 1H), 2.49–2.55(dd, $J = 11.1$, 4.5 Hz, 1H), 2.41–2.42(m, 1H), 2.11–2.15(dd, $J = 11.1$, 1.5 Hz, 1H), 1.98–2.04(m, 2H), 1.64(m, 1H), 1.59(m, 1H); ^{13}C NMR(/ppm): 181.09, 87.22, 77.20, 44.97, 43.50, 38.27, 33.78, 31.64; MS(EI): 155($M^+ + 1$), 137, 126, 108.
4-hydroxy-dihydro-furan-2-one **(12)**: ^{1}H NMR(/ppm): 4.67–4.72(m, 1H), 4.41–4.46(dd, $J = 10.5$, 4.5 Hz, 1H), 4.29–4.33(dd, $J = 10.5$, 1.2 Hz, 1H), 2.73–2.81(dd, $J = 18.0$, 6.0 Hz, 1H), 2.50–2.57(dd, $J = 18.0$, 1.5 Hz, 1H); ^{13}C NMR(/ppm): 176.07, 76.07, 67.80, 38.00; MS(EI): 103($M^+ + 1$), 85.
6-hydroxymethyl-tetrahydro-pyran-2-one **(13)**: ^{1}H NMR(/ppm): 4.35–4.40(m, 1H), 3.61–3.66(m, 2H), 2.26–2.53(m, 2H), 1.40–1.90(m, 4H); ^{13}C NMR(/ppm): 171.38, 80.23, 63.25, 28.55, 22.65, 17.14; MS(EI): 131($M^+ + 1$), 113, 99.
6-(1-hydroxypropyl)-tetrahydro-pyran-2-one **(14)**: ^{1}H NMR(/ppm): 4.19–4.26(m, 1H), 3.46–3.53(m, 1H), 2.40–2.89(m, 2H), 1.51–1.97(m, 6H), 0.95–1.02(t, $J = 7.5$ Hz, 3H); ^{13}C NMR(/ppm): 171.06, 83.04, 74.62, 29.65, 25.58, 24.14, 18.41, 9.91; MS(EI): 159($M^+ + 1$), 141, 123.

(0.40 mmol). The resulting heterogeneous mixture was held at room temperature for 2–20 h, until the ^{1}H spectrum revealed the starting compound was absent. Sodium carbonate was then added to decompose MTO. The product was extracted with ether and washed with a small amount of water. ^{1}H and ^{13}C NMR spectra were obtained from Varian VXR-300 or Bruker DRX-400 spectrometers. Chemical shifts were referenced to Me_4Si. A GC-MS (Varian 3400, Finnegan TSQ 700 triple quadrupole) was used. The spectroscopic data used to identify these products are given in Table 2. The stereochemistry was verified from the ^{1}H-NOE spectra. The ratio of cis and trans isomers was determined by integration of the NMR spectra and from the area of GC peaks.

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