Synthesis Z.-b. Luo et al. PSP

An Efficient and Practical Method for Olefin Dihydroxylation

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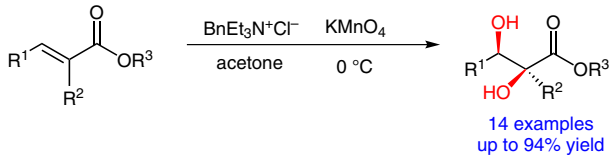

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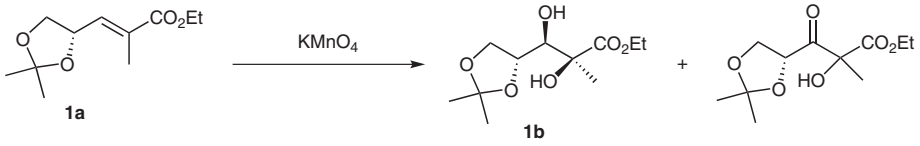
Abstract An efficient and economic procedure was developed for the dihydroxylation of various olefin derivatives with commercial $KMnO_4$ as the oxidant in the presence of a quaternary ammonium salt. This practical procedure is suitable for large-scale production of *cis*-dihydroxy compounds, even those bearing primary and secondary alcohol groups, without overoxidation.

Keyword dihydroxylation, diols, acrylates, alkenes, potassium permanganate, quaternary ammonium salts

Dihydroxylation of olefins is among the most widely used methods for preparing *cis*-dihydroxy compounds, which are useful intermediates for the pharmaceutical and agrochemical industries.[1] One method for olefin dihydroxylation is mediated by osmium salts and is widely used in asymmetric dihydroxylation (AD) to form chiral vicinal diols, as represented by the Sharpless AD reaction.[1b,2] Although this method is widely used in industry, it suffers from the toxicity and the high cost of the osmium salts. A series of Mn and Fe complexes designed to mimic the enzyme-catalyzed mechanism have recently been reported to catalyze the dihydroxylation of olefins.[3] The most conventional method for olefin dihydroxylation is mediated by potassium permanganate,[4] a cheaper and safer reagent. Because of its poor solubility in organic solvents, potassium permanganate is usually used in the form of its aqueous solution. The *cis*-dihydroxylation of alkenes with aqueous alkaline potassium permanganate under low-temperature conditions was reported, but the yields of these reactions were usually unsatisfactory.[4e,5] Hazra et al.[6] reported the dihydroxylation of alkenes with tetradecyl(trimethyl)ammonium permanganate and potassium hydroxide in a two-phase solvent system, or with benzyl(trimethyl)ammonium hydroxide as an organic base in a nonaqueous system. Moderate yields of the *cis*-dihydroxy compounds were realized, but the synthesis of the quaternary ammonium permanganate was difficult to scale up. However, the introduction of quaternary ammonium salts provided a new methodology for dihydroxylations in organic solvents.[7] Brown[8] and Wang[9] and their respective co-workers even realized asymmetric dihydroxylations by using a combination of potassium permanganate and a chiral quaternary ammonium salt.

Recently, during our research on process development for the hepatitis C drug sofubuvir and its intermediates,[10] the efficient synthesis of diol **1b** by dihydroxylation of enoate **1a** was the biggest challenge (Scheme 1). Because of the high toxicity and high cost of osmium tetroxide, the osmium salt methodology was unsuitable for use on an industrial scale. By far the most popular method used in industry is aqueous potassium permanganate-mediated *cis*-dihydroxylation. To achieve a 60–70% isolated yield, the reaction temperature must not exceed –25 °C, which is difficult to realize in a factory. The main byproduct resulted from overoxidation of the secondary hydroxy group in **2b** to form a ketone group. Consequently, suppression of the overoxidation became a key point for the *cis*-dihydroxylation of enoate **1a**. Encouraged by the quaternary ammonium salt concept, we attempted to develop a nonaqueous dihydroxylation protocol.

Here, we describe a new and improved nonaqueous protocol for the *cis*-dihydroxylation of acrylate derivatives. At the beginning, **1a** was chosen as the substrate, with solid potassium permanganate as the oxidant, and we screened various quaternary ammonium salts (QAS) as summarized in Table 1. When no quaternary ammonium salt was used, the isolated yield was low (Table 1, entry 1), and a large amount of the substrate was recovered, possibly due to the low solubility of potassium permanganate in organic solvents. When an aliphatic quaternary ammonium salt such

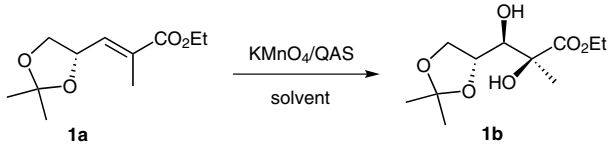


Scheme 1

as tetramethylammonium chloride, tetrabutylammonium chloride, or dodecyl(trimethyl)ammonium chloride was used, better yields were obtained (entries 2, 3, and 6). Quaternary ammonium salts bearing a benzyl group gave even higher yields of the desired product (entries 4 and 5), with benzyl(triethyl)ammonium chloride (TEBAC) giving the best result of all. Because of its cost and availability, TEBAC was used in our subsequent researches. The effects of various conditions, including equivalents of quaternary ammonium salt, reaction temperature, and reaction solvent, are summarized Table 1 (entries 7–16). Acetone was found to be the optimal solvent, and reaction at 0 °C in the presence of 1.2 equivalents of TEBAC proved to be the best conditions. Note that no overoxidation byproduct was observed by TLC, unlike in the oxidation with aqueous potassium permanganate.

Next, the *cis*-dihydroxylation of various acrylate derivatives was examined under the optimized conditions, and the results summarized in Table 2. Acrylate compounds and their derivatives bearing substituents in the 2- and/or 3-positions gave high yields of the corresponding products. Unfortunately, yields from nonfunctionalized olefins under these conditions were no better than those obtained in the absence of TEBAC, and cinnamate compounds gave only trace amounts of the desired dihydroxy products.

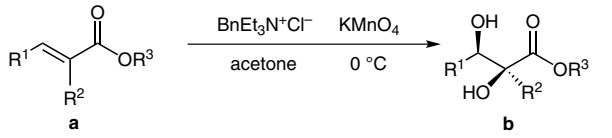
Table 1 Optimization of Conditions for the *cis*-Dihydroxylation of Enoate **1a**[a]



Entry	QAS (equiv)	Temp (°C)	Solvent	Yield[b] (%)
1	–	0	CH_2Cl_2	35
2	Me_4NCl (1.2)	0	CH_2Cl_2	40
3	Bu_4NCl (1.2)	0	CH_2Cl_2	45
4	$BnNMe_3Cl$ (1.2)	0	CH_2Cl_2	65
5	$BnNEt_3Cl$ (1.2)	0	CH_2Cl_2	75
6	$Me(CH_2)_{11}NMe_3Cl$ (1.2)	0	CH_2Cl_2	55
7	$BnNEt_3Cl$ (1.1)	0	CH_2Cl_2	67
8	$BnNEt_3Cl$ (1.0)	0	CH_2Cl_2	60
9	$BnNEt_3Cl$ (1.3)	0	CH_2Cl_2	75
10	$BnNEt_3Cl$ (1.4)	0	CH_2Cl_2	74
11	$BnNEt_3Cl$ (1.2)	25	CH_2Cl_2	68
12	$BnNEt_3Cl$ (1.2)	–10	CH_2Cl_2	76
13	$BnNEt_3Cl$ (1.2)	–20	CH_2Cl_2	75
14	$BnNEt_3Cl$ (1.2)	0	toluene	35
15	$BnNEt_3Cl$ (1.2)	0	EtOAc	69
16	$BnNEt_3Cl$ (1.2)	0	acetone	88

[a] Reaction scale: **1a** (10 mmol), $KMnO_4$ (12 mmol).
[b] Isolated yield.

Table 2 *cis*-Dihydroxylation of Various Alkenes[a]



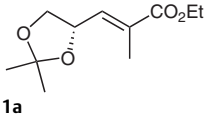
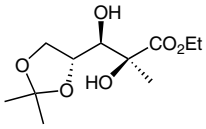
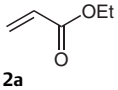
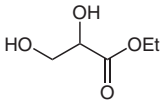
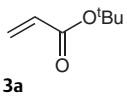
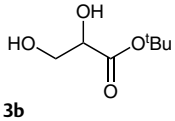
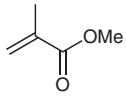
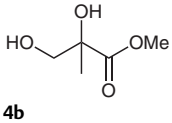
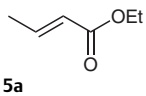
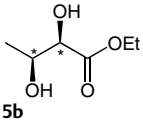
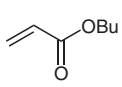
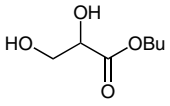
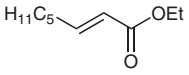
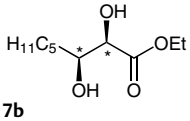
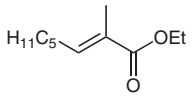
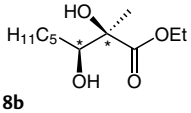
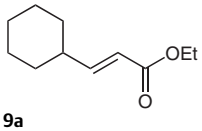
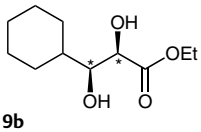
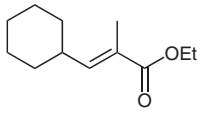
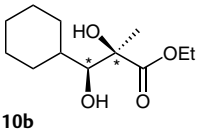
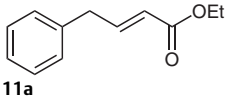
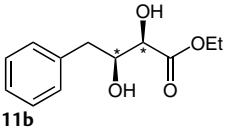
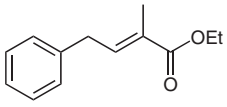
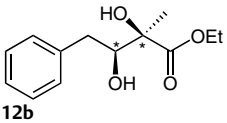
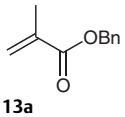
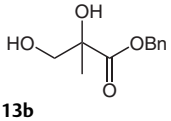
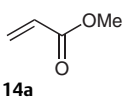
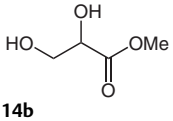
Entry	Alkenes	Product	Yield[b] (%)
1	 **1a**	 **1b**	88[c]
2	 **2a**	 **2b**	90
3	 **3a**	 **3b**	94
4	 **4a**	 **4b**	92
5	 **5a**	 **5b**	88

Table 2 (continued)

Entry	Alkenes	Product	Yield[b] (%)
6	 **6a**	 **6b**	90
7	 **7a**	 **7b**	75
8	 **8a**	 **8b**	72
9	 **9a**	 **9b**	80
10	 **10a**	 **10b**	78
11	 **11a**	 **11b**	86
12	 **12a**	 **12b**	82
13	 **13a**	 **13b**	84
14	 **14a**	 **14b**	90

[a] Reaction conditions: alkene (5 mmol), $KMnO_4$ (6 mmol), TEBAC (6 mmol), acetone (2 mL), –2 to +2 °C.
[b] Isolated yield.
[c] Diastereoselectivity >98:2 (as indicated by ^1H NMR).

The dihydroxylation of **1a** under the optimized conditions was scaled up to 1 mole by using 214 grams of **1a** in the dihydroxylation reaction. Upon addition of **1a**, no significant exothermic change was observed, but the reaction was found to be highly exothermic when quenched with aqueous $NaHSO_3$, indicating that the reaction proceeds via a five-membered-ring complex containing a manganese atom and two oxygen atoms; subsequent cleavage of the Mn–O bond gives the desired OH group on quenching with water. After workup, 211 grams of **1b** were obtained, corresponding to an 85% isolated yield.

In summary, the nonaqueous system TEBAC/$KMnO_4$ induces efficient *cis*-dihydroxylation of acrylate derivatives with high yields under mild conditions. No overoxidation byproducts are formed, probably because the Mn–O bonds in the intermediate five-membered-ring complex serve as protective groups, and the free hydroxy groups are not released until the reaction is quenched with aqueous $NaHSO_3$. All the reagents were cheap and readily available, and the workup procedure was simple and suitable for large-scale production. An asymmetric version of this protocol is under investigation.

Unless otherwise stated, all reagents and solvents were obtained from commercial sources and were used without further purification. Silica gel (200–300 mesh) was used for column chromatography. Analytical TLC was carried out on GF254 commercial silica gel plates. All ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer. IR spectra were recorded on a Nexus 670 FT-IR spectrophotometer. High-resolution mass spectra were recorded in the ESI mode on a Premier CAB088 spectrometer.

α,β-Dihydroxy Esters 1b–14b; General Procedure

TEBAC (6 mmol) and $KMnO_4$ (6 mmol) were mixed in acetone (10 mL), and the mixture was stirred at r.t. for 3 h then cooled to 0 °C. A solution of the appropriate enoate **1a–14a** (5 mmol) in acetone (2 mL) was added dropwise over 5 min while the internal temperature was kept at 5 °C or below. After completion of the addition, the mixture was stirred for a further 30 min at 0 °C until the enoate was completely consumed (TLC). Sat. aq $NaHSO_3$ (5 mL) was added in one portion to quench the reaction, and the mixture was filtered through Celite, which was washed with acetone. The filtrate was concentrated on a rotary evaporator and the residue was extracted with EtOAc. The organic phase was dried (Na_2SO_4), filtered, and evaporated to dryness. The crude oily product was purified by column chromatography (silica gel, 25% EtOAc in PE).

Ethyl (2*S*,3*R*)-3-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2,3-dihydroxy-2-methylpropanoate (1b)[10]

White solid; yield: 1.09 g (88%); mp 75–76 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.20–4.31 (m, 3 H), 4.09 (m, 2 H), 3.93 (d, *J* = 8.0 Hz, 1 H), 2.52 (br s, 2 H), 1.31–1.49 (m, 12 H).

Ethyl *cis*-2,3-Dihydroxypropanoate (2b)[11]

Colorless oil; yield: 0.59 g (90%).

^1H NMR (400 MHz, $CDCl_3$): δ = 4.28 (m, 3 H), 3.88 (m, 2 H), 3.17 (br s, 2 H), 1.30 (m, 3 H).

tert-Butyl *cis*-2,3-Dihydroxypropanoate (3b)[12]

Colorless oil; yield: 0.75 g (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 4.0 Hz, 1 H), 3.83 (dd, *J* = 12.0, 12.0 Hz, 2 H), 2.82 (br s, 2 H), 1.51 (s, 9 H).

Methyl *cis*-2,3-Dihydroxy-2-methylpropanoate (4b)[13]

Colorless oil; yield: 0.61 g (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (m, 4 H), 3.57 (m, 1 H), 3.29 (br s, 2 H), 1.35 (s, 3 H).

Ethyl *cis*-2,3-Dihydroxybutanoate (5b)[14]

Colorless oil; yield: 0.63 g (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 (q, *J* = 8.0 Hz, 2 H), 4.08 (m, 1 H), 4.00 (d, *J* = 4.0 Hz, 1 H), 3.00 (br s, 2 H), 1.30 (m, 6 H).

Butyl *cis*-2,3-Dihydroxypropanoate (6b)[15]

Colorless oil; yield: 0.72 g (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.28–4.22 (m, 3 H), 3.83 (m, 2 H), 3.39 (br s, 2 H), 1.65 (m, 2 H), 1.39 (m, 2 H), 0.94 (t, *J* = 8.0 Hz, 3 H).

Ethyl *cis*-2,3-Dihydroxyoctanoate (7b)[16]

White solid; yield: 0.77 g (75%); mp 41–42 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (q, *J* = 8.0 Hz, 2 H), 4.10 (d, *J* = 2.0 Hz, 1 H), 3.90 (m, 1 H), 2.79 (br s, 2 H), 1.70–1.57 (m, 2 H), 1.56–1.20 (m, 9 H), 0.91 (t, *J* = 8.0 Hz, 3 H).

Ethyl *cis*-2,3-Dihydroxy-3-methyloctanoate (8b)[17]

White solid; yield: 0.78 g (72%); mp 45–46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 (m, 2 H), 3.72 (d, *J* = 12.0 Hz, 1 H), 1.62 (m, 2 H), 1.35 (m, 9 H), 0.90 (t, *J* = 8.0 Hz, 3 H).

Ethyl *cis*-3-Cyclohexyl-2,3-dihydroxypropanoate (9b)[18]

White solid; yield: 0.86 g (80%); mp 50–51 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 (m, 3 H), 3.57 (d, *J* = 8.0 Hz, 1 H), 2.77 (br s, 2 H), 2.07 (m, 1 H), 0.97–1.48 (m, 13 H).

Ethyl *cis*-3-Cyclohexyl-2,3-dihydroxy-2-methylpropanoate (10b)

Colorless oil; yield: 0.9 g (78%);

IR: 3280–3650 (br, m), 2980 (s), 1740 (s), 1250 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 (m, 2 H), 4.0–4.5 (br s, 2 H), 3.62 (d, *J* = 4.0 Hz, 1 H), 1.08–1.92 (m, 17 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.9 (CO), 78.5 (C–O), 77.6 (C–O), 62.3 (–O*C*$H_2$$CH_3$), 42.8 (Cy–C), 38.7 (Cy–C), 28.8 (Cy–C), 26.2 (Cy–C), 26.0 (Cy–C), 25.3 (Cy–C), 22.6 (CH_3), 14.1 (–OCH$_2$*C*H_3).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{12}H_{22}NaO_4$: 253.1416; found: 253.1414.

Ethyl *cis*-2,3-Dihydroxy-4-phenylbutanoate (11b)

White solid; yield: 0.92 g (86%); mp 60–61 °C.

IR: 3060–3550 (br, s), 1750 (s), 1250 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (m, 5 H), 4.27 (m, 2 H), 4.18 (m, 1 H), 4.08 (d, *J* = 2.0 Hz, 1 H), 2.98 (m, 2 H), 2.76 (br s, 2 H), 1.31 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6 (CO), 137.6 (Ar–C), 130.1 (Ar–C), 129.1 (Ar–C), 126.7 (Ar–C), 73.6 (C–O), 72.0 (C–O), 62.1 (–O*C*$H_2$$CH_3$), 40.1 (–*C*Ph), 14.1 (–OCH$_2$*C*H_3).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{12}H_{16}NaO_4$: 247.0946; found: 247.0943.

Ethyl *cis*-2,3-Dihydroxy-3-methyl-4-phenylbutanoate (12b)

White solid; yield: 0.98 g (82%); mp 65–67 °C.

IR: 3050–3530 (br, m), 1750 (s), 1125 (m) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (m, 5 H), 4.27 (m, 2 H), 4.01 (dd, *J* = 2.0, 8.0 Hz, 1 H), 3.03 (dd, *J* = 2.0, 12.0 Hz, 1 H), 2.75 (m, 1 H), 1.47 (s, 3 H), 1.32 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.9 (CO), 138.2 (Ar–C), 129.4 (Ar–C), 128.6 (Ar–C), 126.6 (Ar–C), 76.3 (C–O), 62.2 (–O*C*$H_2$$CH_3$), 36.9 (Ph*C*–), 21.8 ($CH_3$), 14.2 (–OCH$_2$*C*$H_3$).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{13}H_{18}NaO_4$: 261.1103; found: 261.1100.

Benzyl *cis*-2,3-Dihydroxybutanoate (13b)[19]

White solid; yield: 0.88 g (84%); mp 45–46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (m, 5 H), 5.24 (q, *J* = 12.0 Hz, 2 H), 3.85 (d, *J* = 12.0 Hz, 1 H), 3.61 (d, *J* = 12.0 Hz, 1 H), 3.52 (br s, 2 H), 1.37 (s, 3 H).

Methyl *cis*-2,3-Dihydroxypropanoate (14b)[20]

Colorless oil; yield: 0.53 g (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 (t, *J* = 4.0 Hz, 1 H), 3.88 (m, 5 H), 3.01 (br s, 2 H).

Ethyl (2*S,3*R**)-3-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2,3-dihydroxy-2-methylpropanoate (1b); Scaled-Up Synthesis**

A 5 L three-necked round-bottomed flask was charged with TEBAC (273.6 g, 1.2 mol), $KMnO_4$ (189.6 g, 1.2 mol), and acetone (2.14 L), and the mixture was stirred at r.t. for 3 h under N_2 then cooled to –5 to 0 °C. A solution of enoate **1a** (214 g, 1.0 mol) in acetone (214 mL) was added dropwise over 15 min while the internal temperature was kept at 5 °C or below. After completion of the addition, the mixture was stirred for a further 30 min at the same temperature until the enoate was completely consumed (TLC). A solution of $NaHSO_3$ (107 g) in H_2O (214 mL) was added over 5 min to quench the reaction; during the addition the internal temperature was kept at 35 °C or below. The mixture was stirred for 1 h then filtered through Celite, which was washed thoroughly with acetone (3 × 300 mL). The combined filtrates were concentrated under reduced pressure to remove the acetone, and the residue was extracted with EtOAc (3 × 600 mL). The organic phases were combined, washed with brine (2 × 200 mL), dried (Na_2SO_4), filtered, and evaporated to dryness to afford a crude oily product (211 g) that solidified on standing. A 10 g sample of the crude oil was purified by column chromatography (silica gel, 25% EtOAc in PE) to give 9.5 g (81% yield) of the analytically pure product.

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Supporting Information

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