SHORT PAPER

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Vicinal dihydroxylation of alkenes with tetradecyltrimethylammonium permanganate and potassium hydroxide in a two phase solvent system†

Braja G. Hazra*, Vandana S. Pore, Mahendra D. Chordia, Bharat B. Bahule and Sourav Basu

Organic Chemistry Synthesis Division, National Chemical Laboratory, Pune 411008, India

Vicinal *cis*-dihydroxylation of alkenes has been carried out in good yields using tetradecyltrimethylammonium permanganate in a two phase solvent system with an inorganic base present from the beginning of the reaction. With benzyltrimethylammonium hydroxide as an organic base in nonaqueous solvent system reasonably good yields of diols are realised.

Keywords: vicinal dihydroxylation, alkenes

It has been established that the low-temperature oxidation of alkenes with aqueous alkaline potassium permanganate yields mainly 1,2-glycols, by *cis*-hydroxylation. The cyclic manganese (V) ester intermediate is unstable and rapidly hydrolysed at both C–O–Mn bonds, more or less simultaneously to yield diols.[1-3] The yields of diols, however, are seldom above 50% though they can be improved with phase transfer catalysis[4-6] or by increased stirring.[7] The preparation and absorption spectrum of a stable solution of manganese (V) diesters by reacting alkenes with pulverised potassium permanganate in dichloromethane and benzyltriethylammonium chloride as a phase transfer agent has been reported[8,9] by Ogino and his group. It is probable that the intermediate manganate (V) diester is more stable under these conditions because it would be complexed with the quaternary ammonium ion and the hydrolysis reaction would be suppressed by the absence of water. This procedure[8] provided a simple route to a number of diols from alkenes in good yields. The first example of the use of stable cetyltrimethylammonium permanganate salt for the *cis*-dihydroxylation of alkenes has been published[10] by Chandrasekaran and co-workers.

We have recently reported[11,12] the preparation of a relatively stable tetradecyltrimethylammonium permanganate (TDTAP) and its use for the stereoselective and chemoselective *trans*-dibromination and dichlorination of a variety of alkenes. The first practical and acceptable yields of vicinal *cis*-diols from alkenes with TDTAP salt involving the addition of potassium hydroxide in *tert*-BuOH–CH_2Cl_2–H_2O or the use of benzyltrimethylammonium hydroxide as an organic base in a non-aqueous solvent system are presented here.

Treatment of an alkene (1 mmol) in dichloromethane with a solution of TDTAP (1.2 mmol) in dichloromethane for 2 h at 30°C followed by anhydrous or alkaline work-up[10] (Method A), gave poor to moderate yields of diol from the alkenes that we used (Table 1). When the reaction was carried out in aqueous *tert*-butanol followed by treatment with alkali the yield of the diols dropped. Continuing the reaction for a longer period did not improve the yield of diols. In all the cases varying amounts of starting materials were recovered unchanged.

We found that when the reaction was conducted in a two phase solvent system of *tert*-butanol, dichloromethane and water in the ratio 50: 10: 1.25 in the presence of 0.1 mmol of potassium hydroxide (Method C), dihydroxylation occur in good yield. At the start, the pH of the reaction mixture was 7.5 which changed to 9.5 after the addition of aqueous KOH. It remained the same throughout the entire reaction. The beneficial effect of the addition of alkali at the beginning on the yield of diol in $KMnO_4$ oxidation of olefins is well known.[13,14] A delicate balance between the formation of the intermediate cyclic manganese (V) ester, its life time and its instant hydrolysis in alkaline condition (present from the beginning) in a two phase solvent system account for the increased diol formation. The utility of the relatively stable TDTAP salt for the dihydroxylation of a variety of alkenes with aqueous inorganic base has not been reported earlier.

Using benzyltrimethylammonium hydroxide as a base at the beginning in a non-aqueous solvent system of *tert*-butanol and dichloromethane (Method B), gave reasonably good yields of the diols (entries 1–4 in Table 1). Here again the delicate balance between the formation of cyclic ester and its hydrolysis with base soluble in the organic medium[15] is responsible for the formation of the diols in respectable yields. A detailed study of the dihydroxylation of olefins with TDTAP and benzyltrimethylammonium hydroxide as a base in anhydrous homogenous organic medium is documented here for the first time.

TDTAP is a reagent derived from potassium permanganate. It is very much expected that this reagent will add two -OH groups to a double bond like alkaline $KMnO_4$ or OsO_4 to give *cis*-diol from the less hindered side of the double bond. The *exo, cis*-diol **12** is the product of selective oxidation of *endo*-dicyclopentadiene (entry 3, Table 1). It is known[16, 17] that the norbornane double bond of dicyclopentadiene is the more reactive of the two. Again, the dihydroxylation of 3β-acetoxypregna-5,16-dien-20-one (16-dehydropregnenolone acetate, 16 DPA, entry 5, Table 1) takes place on the electron deficient α, β-unsaturated ketone to afford 3β-acetoxy-16α, 17α-dihydroxypregna-5-en-20-one (Compound **14** in Table 1). Potassium permanganate hydroxylation[18] and continuous permanganate oxidation[19] of 3β-acetoxypregna-5, 16-dien-20-one, introduced the two *cis* –OH group at the 16, 17 position from the less hindered side of the double bond to give compound **14**, leaving the 5, 6-double bond unaffected.

In conclusion *cis*-diols were obtained in high yields from the corresponding alkenes using TDTAP, in a biphasic solvent system with an inorganic base or in a homogenous system with an organic base when present from the beginning of the reaction.

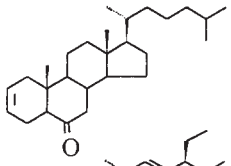
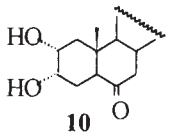
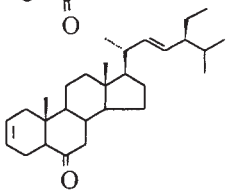
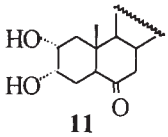
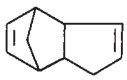
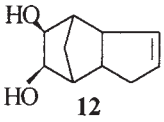
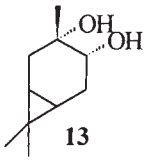
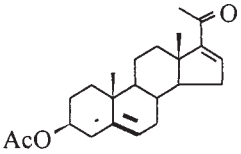
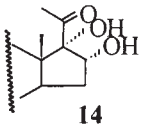
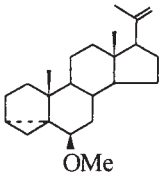
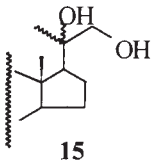
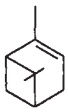
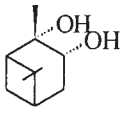
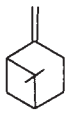
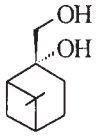
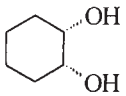
Experimental

All solvents and reagents used were of commercial grade. Reactions were monitored by TLC using TLC aluminium sheets, [silica gel

* To receive any correspondence. E-mail: hazra@ems.ncl.res.in

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1

Entry	Alkene	Diol	Method	Yield/%
1		 **10**	A B C	21 51 73
2		 **11**	A B C	29 56 76
3		 **12**	A B C	44 83 78
4		 **13**	A B C	27 47 71
5		 **14**	A C	21 50
6		 **15**	A C	32 75
7		 **16**	A C	39 56
8		 **17**	A C	44 62
9		 **18**	A C	45 69

$60F_{254}$ precoated, Merck, Germany]. The spots were located by spraying with ethanolic solution of phosphomolybdic acid followed by heating. Usual workup means the organic extract was thoroughly washed with water and brine and finally dried over anhydrous sodium sulfate. -IR: Perkin-Elmer 599B. -^{1}H NMR: Bruker AC 200 (200 MHz)/ AC 300 (300 MHz). –Optical rotations : JASCO Digital Polarimeter using sodium light (λ = 5893 °A) source. -MS: Finnigan 1020C (70eV). Melting points (uncorrected): Yanaco Micro melting point apparatus.

General procedure: *Method A:* A solution of cholest-2-en-6-one **1** (0.384 g, 1 mmol) in dichloromethane (12 ml) was added to a stirred solution of TDTAP (0.420 g, 1.12 mmol) in dichloromethane (10 ml). The reaction mixture was stirred for 2 h at 30°C. It was then treated with 5% aqueous NaOH (5 ml), stirred for 30 minutes. The solvent was evaporated and the residue was extracted with ethyl acetate. The extract was washed with water and brine, dried (Na_2SO_4) and filtered. Concentration of the filtrate followed by column chromatography over silica gel afforded pure cholest-2α,3α-diol-6-one **10** (0.088 g,

21%) and starting material (0.204 g, 69%) was recovered. (Carrying out the reaction in aqueous *tert*-butanol followed by treatment with alkali gave even lower yield.)

Method B: A solution of cholest-2-ene-6-one **1** (0.384 g, 1 mmol) in *tert*-BuOH (8 ml) and CH_2Cl_2 (4 ml) was added to benzyltrimethylammonium hydroxide (0.334 g, 2 mmol). To this magnetically stirred mixture, TDTAP (0.420 g, 1.12 mmol) was added in small portions during 2 min at 30°C. The reaction mixture was stirred at this temperature for 1 h and then quenched with saturated aqueous solution of sodium bisulphite solution (10 ml). The mixture was stirred for another 30 min. The solvent was evaporated off and the residue was extracted with ethyl acetate (3 × 25 ml). The combined extracts were washed with water followed by saturated brine, dried (Na_2SO_4) and filtered. Concentration of the filtrate followed by column chromatography over silica gel afforded pure cholest-2α,3α-diol-6-one **10** (0.213 g, 51%) and starting material (0.047 g, 16%) was recovered.

Method C: To a magnetically stirred solution of cholest-2-ene-6-one **1** (0.384 g, 1 mmol) in *tert*-BuOH (10 ml) and CH_2Cl_2 (2 ml) at 30°C was added a solution of KOH (0.006 g, 0.1 mmol) in water (0.5 ml) followed by TDTAP (0.420 g, 1.12 mmol) in small portions during five min. The reaction mixture was stirred at this temperature for 1 h and then quenched with saturated aqueous solution of sodium bisulphite solution (10 ml). The mixture was stirred for another 30 min. The solvent was evaporated off and the residue was extracted with ethyl acetate (3 × 25 ml). The combined extracts were washed with water followed by saturated brine, dried (Na_2SO_4) and filtered. Concentration of the filtrate followed by column chromatography over silica gel afforded pure cholest-2α,3α-diol-6-one **10** (0.305 g, 73%).

2α, 3α-Dihydroxy-5α-cholest-6-one **10:** White crystalline solid, m.p. 202–204°C (from hexane-ethyl acetate; lit.[15] 206-207°C); γ_{max} / cm^{-1} 3360 (OH), 1720 (C=O); δ H (200 MHz : $CDCl_3$: Me_4Si) 0.65 (3H, s, 18-CH_3), 0.75 (3H, s, 19-CH_3), 0.84 (6H, d, *J* = 6 Hz, 26 and 27-CH_3), 0.89 (3H, d, *J* = 5 Hz, 21-CH_3), 3.71 (1H, m, 2-CH), 4.02 (1H, m, 3-CH); $[\alpha]^{30}_D$ = +6.8° (c = 0.6, $CHCl_3$).

2α, 3α-Dihydroxy-24S-ethyl-5α-cholest-22E-en-6-one **11**: White needles, m.p. 232–234°C (from ethanol, lit.[20] 235-238°C); γ_{max} / cm^{-1} 3360 (OH), 1715 (C=O); δ H (200 MHz : $CDCl_3$: Me_4Si) 0.70 (3H, s, 18-CH_3), 0.76-0.90 (12H, merging 1s 19-CH_3, 2d 26 and 27-CH_3, 1t 29-CH_3), 1.02 (3H, d, *J* = 7 Hz, 21-CH_3), 2.72 (1H, dd, *J* = 12 and 3 Hz, 5-CH), 3.78 (1H, m, 2-CH), 4.06 (1H, m, 3-CH), 5.13 (2H, m, 22 and 23-CH); $[\alpha]^{28}_D$ = –9.7° (c = 1.004, $CHCl_3$).

5-exo, 6-exo-Dihydroxy-endo-3a, 4, 5, 6, 7, 7a-hexahydro-4, 7-methano-indene **12**: Low melting solid, m.p. 50–51°C (from light petrolium, lit.[17] 48–51°C); γ_{max} / cm^{-1} 3373 (OH); δ H (300 MHz : $CDCl_3$: Me_4Si) 1.28 (1H, m, 3a-CH), 1.84 (1H, m, 4-CH), 2.07 (1H, m, 7-CH), 2.23–3.05 (7H, m, 3, 7a, 8 and 2-OH), 3.69 (1H, m, 5/6-CH), 3.77 (1H, m, 5/6-CH), 5.58 (2H, m, 1 and 2-CH).

3α, 4α- Caranediol **13**: Low melting solid, m.p. 68°C (from hexane, lit.[21] 70–71°C); γ_{max} / cm^{-1} 3400 (OH), 1385, 1080, 1060, 935, 870; δ H (200 MHz : $CDCl_3$: Me_4Si) 0.65 (2H, m, 1 and 6-CH), 0.90 (3H, s, 10-CH_3), 1.15 (3H, s, 8/9-CH_3), 1.22 (3H, s, 9/8-CH_3), 2.05 (4H, m, 2 and 5-CH_2), 3.21 (1H, dd, *J* = 10, 2 Hz, 3-CH).

3β-Acetoxy-16α, 17α-dihydroxypregn-5-en-20-one **14**: White solid, m.p. 191°C (from methanol, lit.[19] 193-195°C); γ_{max} / cm^{-1} 3419 (OH), 1737 (O-C=O), 1695 (C=O); δ H (200 MHz : $CDCl_3$: Me_4Si) 0.66 (3H, s, 18-CH_3), 0.99 (3H, s, 19-CH_3), 2.01 (3H, s, 21-CH_3), 2.22 (3H, s, 3-OAc), 3.85 (1H, m, 16-CH), 4.59 (1H, m, 3-CH), 5.36 (1H, m, 6-CH); $[\alpha]^{30}_D$ =-51.8° (c = 1.2, $CHCl_3$).

3α, 5-Cyclo-6β-methoxy-20, 22-dihydroxypregnane **15**: Yellowish oil, γ_{max} / cm^{-1} 3410 (OH), 1390, 1105, 870, 850; δ H (200 MHz : $CDCl_3$: Me_4Si) 0.90 (3H, s, 18-CH_3), 1.05 (3H, s, 19-CH_3), 1.28 (3H, s, 21-CH_3), 2.82 (1H, t, *J* = 3 Hz, 6-CH), 3.36 (3H, s, -OCH_3), 3.25–3.8 (2H, m, 22-CH_2); *m/z* 362 (M^+ , 4), 347(18), 331(91), 307(25), 299(33), 281(34), 213(25), 199(41), 159(50), 145(34), 131(35), 121(37), 105 (100%), 91(99), 79(80), 71(45), 67(23), 57(12); Found : C, 75.91; H, 10.83. Calc. for $C_{23}H_{38}O_3$ (362) : C, 76.24; H, 10.50%.

Pinane-2α, 3α-diol **16**: Low melting solid, m.p. 54°C (from hexane, lit.[22] 55–56°C); γ_{max} / cm^{-1} 3400 (OH), 1380, 1230, 1100, 1060, 1030, 960, 920; δ H (200 MHz : $CDCl_3$: Me_4Si) 0.93 (3H, s, 8/9-CH_3), 1.26 (3H, s, 9/8-CH_3), 1.29 (3H, s, 10-CH_3), 1.33–2.65 (6H, m, 1 and 5-CH, 4 and 6-CH_2), 3.96 (1H, dd, *J* = 9 and 5 Hz, 3-CH); *m/z* 170 (M^+, <1), 152(1), 137(3), 126(34), 111(39), 99 (100%), 93(21), 81(33), 71(74), 55(36), 43(86).

Pinane-2α, 10-diol **17**: White solid, m.p. 82°C (from diethyl ether-hexane, lit.[23] 83–85°C); γ_{max} / cm^{-1} 3380 (OH), 1385, 1220, 1185, 1040; δ H (200 MHz : $CDCl_3$: Me_4Si) 0.91 (3H, s, 8/9-CH_3), 1.22 (3H, s, 9/8-CH_3), 1.40–3.17 (10H, m, 1 and 5-CH, 3, 4 and 6-CH_2 and 2-OH), 3.50 (2H, s, 10-CH_2); *m/z* 170 (M^+, <1)), 152(1), 139(55), 121(29), 109(9), 93(17), 83 (100%), 69(95), 55(67), 41(56).

cis-Cyclohexane-1, 2-diol **18**: White crystalline solid, m.p. 96°C (from diethyl ether, lit.[24] 98°C); γ_{max} / cm^{-1} 3400 (OH), 1490, 1480, 1225; δ H (200 MHz : $CDCl_3$: Me_4Si) 1.05–2.0 (8H, m, 3, 4, 5 and 6-CH_2), 3.72 (2H, bd, 1 and 2-CH).

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