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A facile synthesis of vicinal *cis*-diols from olefins catalyzed by *in situ* generated Mn_xO_y nanoaggregates†‡

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A novel protocol for the practical and green synthesis of vicinal *cis*-diols from 10.0 mmol olefins by using 5.0 mmol $KMnO_4$ as oxidant and 30.0 mmol H_2O_2 as co-oxidant is reported. The presented procedure is easy to carry out and enables the direct transformation of linear and cyclic alkenes to the corresponding vicinal *cis*-diols. The synthesis of vicinal *cis*-diols by dihydroxylation of olefins with a $KMnO_4/H_2O_2$ system was catalyzed by *in situ* generated Mn_xO_y nanoaggregates. The use of H_2O_2 as a co-oxidant is the key for the protocol to synthesize vicinal *cis*-diols in high yields, because it assists the oxidation of Mn_xO_y nanoaggregates, which have an active role in the oxidation reaction medium.

Polyhydroxyl alcohols are industrially important compounds, as some of their derivatives are used in the production of several natural products and drugs.[1] The cyclitols, especially molecules bearing three or more hydroxyl groups, constitute an important class of compounds in synthetic organic chemistry. Vicinal *cis*-diols are the most important functional group in cyclitols, as they are an important component of many drugs and show significant biological activities.[1] Besides their biological activities, they can also be used as solvents in the cleaning, cosmetic and pharmaceutical industries.[2] Therefore, studies on the practical and green synthesis of vicinal *cis*-diols have gained great importance. Although various methods have been developed for the synthesis of vicinal *cis*-diols, the most convenient method is the oxidation of olefins in the presence of a suitable oxidant.[3] Oxidation systems including (i) stoichiometric OsO_4, (ii) a metal oxide and a co-oxidant such as OsO_4/NMO or $RuCl_3/NaIO_4$, (iii) excess $KMnO_4$, and (iv) organometallic complexes, have been used in the synthesis of vicinal *cis*-diols.[4] Among these protocols, OsO_4/co-oxidant catalyzed olefin oxidation is one of the most powerful routes.

In spite of the widespread application of this type of reaction in synthetic organic chemistry, the high cost, volatility and hazardous toxicity of OsO_4, along with the problem of contamination, are the main drawbacks for use in industry, when the principles of green chemistry are considered.[5] Given the economic and environmental restrictions, a protocol that uses more environmentally-friendly reactants such as $KMnO_4$, H_2O_2 and molecular oxygen in the oxidation of olefins is highly desired.[6] $KMnO_4$ has been used as a strong oxidant not only in medicinal applications,[7] but also in several specific organic reactions, such as *cis*-dihydroxylation,[8] epoxidation,[9] and deoxidisation[10] at low temperatures. In the green synthesis of vicinal *cis*-diols by dihydroxylation of olefins, $KMnO_4$ was generally used in more than one equivalent, and several undesired by-products were produced.[11] These previous studies revealed that various manganese oxide derivatives could be formed during oxidation reactions in the presence of $KMnO_4$ as oxidant.[12]

In this study, we report a novel protocol for the practical and green synthesis of vicinal *cis*-diols. The dihydroxylation of olefins was performed in the presence of 5.0 mmol of $KMnO_4$ (0.5 eq.) as oxidant and 30.0 mmol of hydrogen peroxide (3.0 eq.) as co-oxidant in a water–acetone mixture ($v/v = 1:2$). Compared to methods reported in the literature, our protocol provides shorter reaction times, higher yields and a greener approach, by using a smaller amount of $KMnO_4$ for the synthesis of vicinal *cis*-diols.[12,13] Various cyclic and linear olefins were oxidized using our new protocol. Besides the high-yield synthesis of vicinal *cis*-diols, various manganese oxide derivatives were formed *in situ* during the oxidation reaction, among which Mn_3O_4 nanoaggregates were determined to be the main component. The Mn_3O_4 nanoaggregates were characterized using several advanced analytical techniques (TEM, SEM, XRD, XPS, EDX, BET and BJT). The results revealed that the use of

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† Dedicated to Prof. Dr Metin Balci in recognition of his contribution to organic chemistry, on the occasion of his retirement.

‡ Electronic supplementary information (ESI) available: General procedure for synthesis of vicinal *cis*-diols. See DOI: 10.1039/c5ra01646k

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Table 1 Vicinal *cis*-dihydroxylation of various olefins (10.0 mmol) by 5.0 mmol $KMnO_4$ in the presence of 30.0 mmol H_2O_2 as co-oxidant[a]

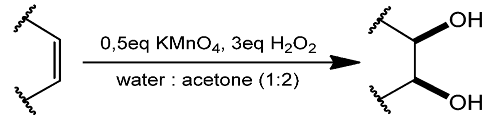
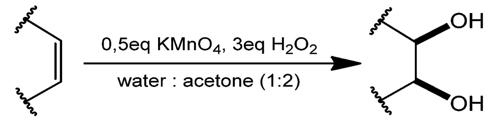
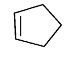
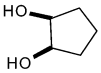
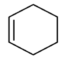
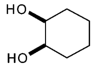
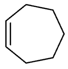
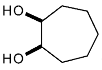
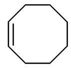
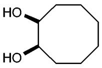
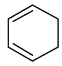
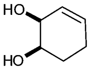
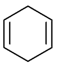
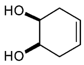
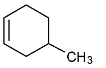
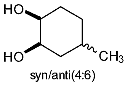
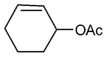
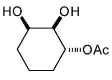
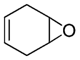
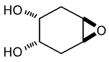
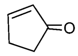
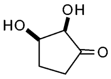
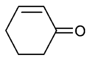
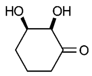
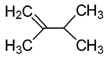
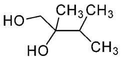
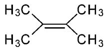
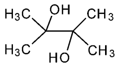
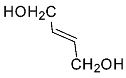
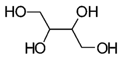
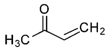
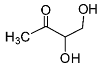
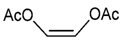
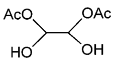
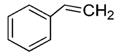
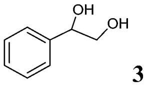
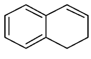
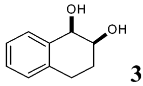
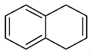
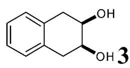
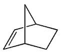
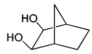


Table 1 (*Contd.*)



Entry	Olefin	Vicinal *cis*-diol	Isolated yields (%), 2 h		
			RT	0 °C	0 °C, N_2
1	 **1**	 **2**	51	77	82
2	 **3**	 **4**	50	78	95
3	 **5**	 **6**	67	75	90
4	 **7**	 **8**	56	73	79
5	 **9**	 **10**	33	47	60
6	 **11**	 **12**	58	65	72
7	 **13**	 **14a,b**	58	65	72
8	 **15**	 **16**	62	75	83
9	 **17**	 **18**	31	42	65
10	 **19**	 **20**	43	52	75
11	 **21**	 **22**	41	50	63
12	 **23**	 **24**	47	58	62
13	 **25**	 **26**	49	60	66
14	 **27**	 **28**	45	54	60
15	 **29**	 **30**	60	66	76
16	 **31**	 **32**	50	57	68
17	 **33**	 **34**	52	63	70
18	 **35**	 **36**	62	73	82
19	 **37**	 **38**	65	73	85
20	 **39**	 **40**	43	52	73

[a] Reaction conditions: all dihydroxylation reactions were performed in aqueous acetone (20.0 mL, water–acetone = 1 : 2 v/v) using 5.0 mmol $KMnO_4$, 10.0 mmol olefin, and 30.0 mmol H_2O_2.

H_2O_2 as a co-oxidant is the key for the protocol to synthesize vicinal *cis*-diols in high yields, because it assists the oxidation of Mn_3O_4 nanoaggregates, which have an active role in the oxidation reaction medium. We thought that the oxidation reaction continues because the transformation of manganese oxide derivatives into manganese dioxide is delayed in the hydrogen peroxide reaction medium.

The amount of H_2O_2 in the oxidation reaction was optimized by performing dihydroxylation reactions using different amounts of H_2O_2 with 5.0 mmol $KMnO_4$ in a water–acetone (v/v = 1 : 2) mixture (see methods and Table S1 in the ESI‡). Acetone and water are especially applicable for these oxidation reactions. Acetone is immiscible with water and serves as an important solvent, so an acetone–water solvent mixture is a useful solvent for the $KMnO_4$ oxidation reaction, and tap water is used in our protocol for practical purposes. Under the optimized reaction conditions, maximum yields were obtained using 10.0 mmol of olefin, 5.0 mmol of $KMnO_4$ and 30.0 mmol of H_2O_2 in aqueous acetone (H_2O–acetone, v/v = 1 : 2) at 0 °C and under a nitrogen atmosphere (Table 1, entries 1–20). Additionally, in our protocol, hydrogen peroxide is the driving force for the dihydroxylation of olefins, and should be used carefully in this reaction medium. It is important to note that the nitrogen atmosphere and low temperature (0 °C) conditions greatly influence the yield of the dihydroxylation reaction. The results of this study show that the presence of O_2 is closely related to the yields of the dihydroxylation reaction, as can be seen from Table 1.

Taking these results into account, it might be assumed that several manganese oxide derivatives are formed *in situ* during

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the oxidation reaction and catalyze the oxidation of olefins. To elucidate this phenomenon, the dark brown/blackish solid material was separated from the reaction medium, washed and dried under vacuum, and then characterized by TEM (transmission electron microscopy), SEM (scanning electron microscopy), XPS (X-ray photoelectron spectroscopy), XRD (X-ray diffraction), EDX (energy-dispersive X-ray spectroscopy), BET (Brunauer Emmett Teller) and BJT (bipolar junction transistor) adsorption analyses. Fig. 1A shows a representative TEM image of the recovered brown/blackish solid material. The TEM image reveals the formation of nanoaggregates from small spherical nanoparticles (∼300 nm). The formation of nanoaggregates from small nanoparticles can also be seen from a representative SEM image of the material shown in Fig. 1B. Additionally, the SEM image indicates the porous structure of the material, which is very important for heterogeneous catalysis applications. The Mn_3O_4 structure can also be identified by the XRD pattern of the solid material. Fig. 1C shows representative XRD spectra for pure Mn_3O_4 and for the Mn_xO_y nanoaggregates. Hence, we concluded that the solid material recovered at the end of the oxidation reaction was formed by the aggregation of mostly Mn_3O_4 nanoparticles, along with other Mn_xO_y derivatives. Additionally, Mn_3O_4 formed in the reaction medium reacted again with H_2O_2, and the olefin was converted to vicinal *cis*-diol, while some of the Mn_3O_4 was converted into MnO_2, which was observed by a color change from blackish to brown.

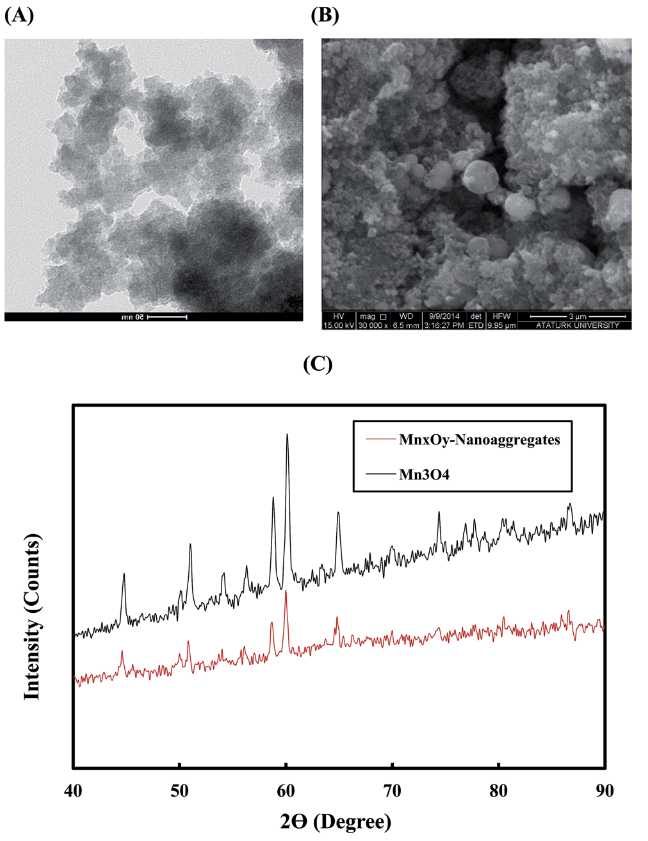

Fig. 1 (A) TEM image; (B) SEM image; (C) XRD pattern spectrum of the solid material recovered at the end of the oxidation reaction.

The porous structure and surface area of the material were further analyzed by BET-surface area measurement and BJT adsorption analyses. The BET analysis confirmed that the recovered material had a surface area of 129.6 ± 0.6 $m^2 g^{-1}$; the average pore radius of the material was measured as 4.6 nm, and the cumulative surface area of the pores was found to be 117.4 $m^2 g^{-1}$ by BJT adsorption analysis (see FS-1 in ESI‡). The elemental composition of the Mn_xO_y nanoaggregates was determined by EDX analysis. EDX spectra showed the presence of manganese as well as oxygen, carbon and potassium atoms. (see, FS-2 in ESI‡).

Besides the morphology of the material, we studied its XPS spectra to clarify its chemical composition (Fig. 2). The survey XPS spectrum (Fig. 2A) of the material indicates the presence of Mn along with other elements K, Cl and O; the Cl might be due to the water used in the experiments. Fig. 2B shows the deconvoluted XPS spectra for the $Mn2p_{3/2}$ and $Mn2p_{1/2}$ core levels at 641.1 eV and 652.8 eV, respectively. The deconvoluted spectra reveal that the material includes oxidized Mn derivatives and no metallic Mn. The oxide species were found to be mostly Mn_3O_4 and MnO_2, along with the other possible manganese oxide species in small fractions.[14] This conclusion was also supported by the high-resolution XPS spectrum of the Mn3s core level (Fig. 2C), in which the distance of 4.8 eV between the two peaks observed for the Mn3s core level indicates that the material consists mainly of Mn_3O_4.

Instead of starting with $KMnO_4$, commercial MnO_2 (Sigma-Aldrich code no. 63548), Mn_3O_4 (Sigma-Aldrich code no. 377473) and the Mn_xO_y nanoaggregates formed in the reaction medium were tested under the optimized reaction conditions. In these test reactions, the procedure (0 °C, N_2 atm.) was applied to cylohexene (**3**), 3-buten-2-one (**29**) and styrene (**33**) molecules in the presence of commercial MnO_2, Mn_3O_4 and *in situ* generated Mn_xO_y nanoaggregates. No vicinal *cis*-diols were obtained from the reaction of 10.0 mmol olefin with 5.0 mmol MnO_2 and 30.0 mmol H_2O_2, whereas the corresponding vicinal *cis*-diols were obtained using Mn_3O_4. When we used 30.0 mmol H_2O_2 in the dihydroxylation reaction together with 5.0 mmol Mn_3O_4 and 10.0 mmol olefin (**3**, **29** or **33**), the yields of the corresponding vicinal *cis*-diols (**4**, **30** and **34**) were low (25, 22 and 20%, respectively). A certain amount of olefin was converted to decomposition products, which were not identified. Because of the low yields and the decomposition of olefins in this test reaction, we used 10.0 mmol H_2O_2, 5.0 mmol Mn_3O_4 and 10.0 mmol olefin, and better yields were obtained (about 34% for **4**, 30% for **30**, and 27% for **34**) under the same reaction conditions. When we used 10.0 mmol olefin (**3**, **29** or **33**) with 30.0 mmol H_2O_2 and 0.4 g of the dark brown/blackish solid residue material (Mn_xO_y nanoaggregates) formed in the reaction medium, vicinal *cis*-diols (**4**, **30** and **34**) were obtained in yields of about 42% for **4**, 40% for **30**, and 36% for **34** under the same reaction conditions (see methods and Table S2 in the ESI‡).

In summary, we can conclude that the Mn_xO_y oxide derivatives, mainly Mn_3O_4 nanoaggregates, were generated *in situ* from $KMnO_4/H_2O_2$ during the synthesis of vicinal *cis*-diols from olefins. It is thought that the Mn_3O_4 formed in the reaction medium has a major role in the further oxidation reaction.

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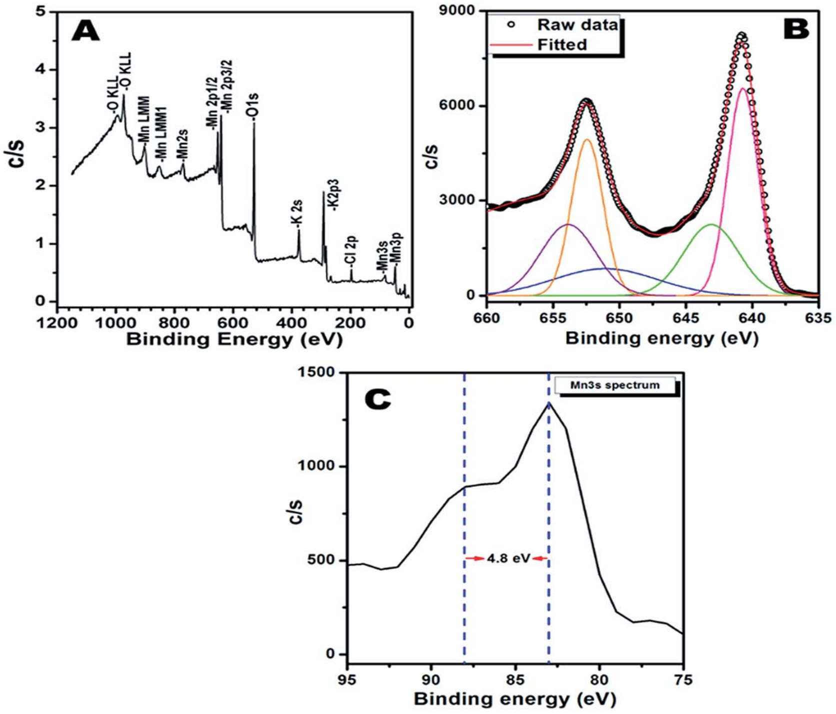
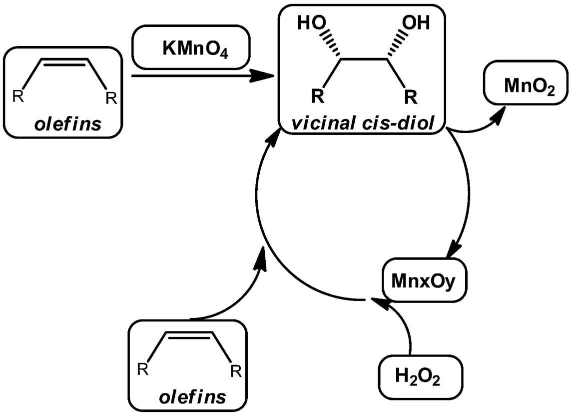


Fig. 2 XPS spectra of the solid material recovered at the end of the oxidation reaction.

Scheme 1 shows the proposed mechanism for the dihydroxylation reaction in aqueous acetone. In the first step of the oxidation reaction, olefins are oxidized by $KMnO_4$ in aqueous acetone and the expected vicinal *cis*-diols, along with Mn_xO_y derivatives, are formed. In the second step, oxygen atoms are transferred from H_2O_2 to the Mn_xO_y residue having Mn_3O_4 nanoaggregates as a main component.[15] Following this, vicinal *cis*-diols are obtained by ensuring the continuous oxidation of Mn_3O_4 by H_2O_2.

Table 1 shows the results of the dihydroxylation of cyclic and linear olefins using our novel protocol (see ESI‡ for experimental details). Cyclic mono-alkenes (**1**, **3**, **5**, **7**, **35** and **37**, entries 1–4 and 18–19) have been demonstrated to be very active, and the respective vicinal *cis*-diols (**2**, **4**, **6**, **8**, **36** and **38**) were obtained in high yields (79–95%). On the other hand, molecules bearing diene groups (**9** and **11**) were selective for mono-dihydroxylation, and the corresponding alkene-diol compounds (**10** and **12**) were obtained in yields of 60% and 72%, respectively. Methyl-, acetoxy- and epoxy-substituted olefins (**13**, **15** and **17**) were disposed to dihydroxylation, in which **15** and **17** were converted to stereospecific products (**16** and **18**) in yields of 83% and 65%, respectively. On the other hand, 4-methyl-1-cyclohexene (**13**) gave *syn* and *anti*-isomer products (ratio *syn* : *anti* 45 : 55). Cyclic α,β-unsaturated carbonyl compounds such as cyclopentenone (**19**) and cyclohexenone (**21**) were converted directly to the corresponding vicinal *cis*-diols (**20** and **22**, respectively) in yields of 75% and 63%. Linear olefins (Table 1, entries 12–17) were easily transformed to the respective vicinal *cis*-diols (**24**–**34**) in good yields (60–76%). Norbornene (**39**) reacted easily and was converted to the *exo*-*cis*-diol **40** in a good yield of 73%. Some of the vicinal *cis*-diols were identified by ^{1}H and ^{13}C-NMR spectroscopy by comparison with the literature data.[5]



Scheme 1 A proposed mechanism for the dihydroxylation of 10.0 mmol olefins by 5.0 mmol $KMnO_4$/30.0 mmol H_2O_2 in aqueous acetone.

To examine the effect of an inert atmosphere on our protocol, we performed the dihydroxylation of all olefins at 0 °C under N_2 gas. The results revealed that vicinal *cis*-diols were obtained in higher yields than when the reactions were carried out under air. It can be concluded that an inert atmosphere is more effective for the controlled oxidation of Mn_xO_y derivatives, especially Mn_3O_4 nanoaggregates, in the dihydroxylation reaction of olefins.

In conclusion, we have developed a novel and facile oxidation system for the dihydroxylation of olefins to vicinal *cis*-diols.

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The present $KMnO_4/H_2O_2$ oxidation system provides many advantages, such as being eco-friendly,[6] using fewer equivalents of $KMnO_4$, and *in situ* generation of the catalyst. Moreover, the reported procedure is easy to carry out and enables the direct transformation of linear as well as cyclic alkenes to the corresponding vicinal *cis*-diols. In addition, we believe that this study will give new insights to materials chemists on the synthesis of Mn_xO_y nanoaggregates, mainly Mn_3O_4. Furthermore, the lifetime of the Mn_xO_y by-products obtained from $KMnO_4$ can be elongated using various oxidants. By delaying the formation of MnO_2 in this way, the functionality of the Mn_xO_y by-product can be increased.

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