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Article

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

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

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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 corresponding vicinal *cis*-diols. Applicable synthesis of vicinal *cis*-diols from the dihydroxylation of olefins with $KMnO_4/H_2O_2$ 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 at high yields because it assists the oxidation of Mn_xO_y nanoaggregates which has active role in the oxidation reaction conditions.

Polyhydroxyl alcohols are industrially important compounds that their some derivatives take place in the production of several natural and drug materials.¹ Particularly, cyclitols that are the molecules bearing two or more hydroxyl groups and generally found in natural products constitute an important class of synthetic organic chemistry. A functional group of the cyclitols, the vicinal *cis*-diols are the most important ones because they are important component of many drugs and they show significant biological activities.¹ Besides their biological activities, they can also be used as solvent in cleansing, cosmetic, pharmaceutical industry.² Therefore, the studies on 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 one is the olefin oxidation in the presence of a suitable oxidant.³ The oxidation systems including (i) stoichiometric OsO_4 (ii) a metal oxide and a co-oxidant such as OsO_4/NMO and $RuCl_3/NaIO_4$, (iii) excess $KMnO_4$, and (iv) organic metal complexes have been used in the synthesis of vicinal *cis*-diols.⁴ Among those protocols, the OsO_4 /co-oxidant catalyzed olefin oxidations is one of the most powerful route.

In spite of the widespread application of this type of reactions in synthetic organic chemistry, the high cost, volatility and hazardous toxicity of OsO_4 along with the contamination problem are the main drawbacks for their use in industry on the subject of the green chemistry.⁵ Considering 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 applications⁷ but also in several specific organic reactions such as *cis*-dihydroxylation,⁸ epoxidation,⁹ deoximisation¹⁰ at low temperatures. In the green synthesis of vicinal *cis*-diols from the dihydroxylation of olefins, $KMnO_4$ was generally used more than one equivalent and several undesired by-products were produced.¹¹ Those studies revealed that various manganese oxide derivatives could be formed during the 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 eqv.) as an oxidant and 30.0 mmol of hydrogen peroxide (3.0 eqv.) as a co-oxidant in water-acetone mixture ($v/v=1/2$). Compared to ones reported in the literature, our protocol provides shorter reaction times, higher yields and more green approach by using less amount of $KMnO_4$ for the synthesis of vicinal *cis*-diols.¹² Various cyclic and linear olefins were oxidized by using our new protocol. Besides high-yield synthesis of vicinal *cis*-diols, various manganese oxide derivatives were formed in-situ during the oxidation reactions, in which the Mn_3O_4 nanoaggregates are determined to be the main component of them. The Mn_3O_4 nanoaggregates were characterized by using several advanced analytical techniques (TEM, SEM, XRD, XPS, EDX, BET and BJT). The results revealed that the use of H_2O_2 as a co-oxidant is the key for the protocol to synthesize vicinal *cis*-diols at high yields because it assists the oxidation of Mn_3O_4 nanoaggregates which has active role in the oxidation reaction medium. We think oxidation will continue by delaying the transformation of manganoxide derivatives into mangandioxide in hydrogenperoxide reaction medium.

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H₂O₂ amount in the oxidation reaction were optimized by performing the dihydroxylation reactions by using different amounts of H₂O₂ with 5.0 mmol KMnO₄ in water /acetone (v/v=1:2) mixture (see methods and table S1 in the ESI). Especially, acetone and water are applicable materials for these oxidation reactions. Acetone is miscible with water and serves as an important solvent, so acetone-water solvent mixture useful solvent in KMnO₄ oxidation reaction and the water is used as a tap water for practically use in our protocol. According to optimized reaction conditions, the maximum yields were obtained by using 10 mmol of olefin, 5.0 mmol KMnO₄ and 30.0 mmol of H₂O₂ in aqueous acetone (H₂O/acetone (v/v)=1/2) at 0 °C and under nitrogen atmosphere (Table-1, entries 1-20). Additionally, in our protocol, the hydrogen peroxide is driving-force for this dihydroxylation reaction of olefins and should be carefully used in this reaction media. It is important to note that nitrogen atmosphere and low temperature (0 °C) in reaction condition are greatly influenced to yield of dihydroxylation reaction. The results of present study show that the O₂ is closely related to yields of dihydroxylation reaction as shown in Table-1.

Table 1. Vicinal *cis*-dihydroxylation of various olefins (10 mmol) by 5.0 mmol. KMnO₄ in the presence of 30.0 mmol H₂O₂ as co-oxidant

TABLE-1

Reaction conditions: All dihydroxylation reactions were performed in aqueous acetone (20.0 mL, water–acetone= 1: 2 v/v) using 5.0 mmol KMnO₄, 10.0 mmol olefin, and 30.0 mmol H₂O₂.

By taking these results into account, it might be assumed that several manganese oxide derivatives formed in-situ during the oxidation reaction and catalyzed the oxidation of olefins. To elucidate this phenomenon, the dark brown/blackish solid material was separated from the reaction medium, washed off and dried under vacuum and then characterized by TEM (transmission electron microscopy), SEM (scanning electron microscope), XPS (X-ray photoelectron spectroscopy), XRD (X-ray diffraction), EDX (Energy-dispersive X-ray spectroscopy), BET (BET from Brunauer, Emmett, Teller) and BJT (bipolar junction transistor) adsorption analyses. Figure 1A shows a representative TEM image of the recovered brown/blackish solid material. TEM image reveals the formation of nanoaggregates from small spherical nanoparticles (~300 nm). The nanoaggregates formation by small nanoparticles can also be seen by a representative SEM image given for the material in Figure 1B. Additionally, the SEM image indicates the porous structure of the material, which is very important for the heterogeneous catalysis applications. The Mn₃O₄ structure can also be identified by XRD pattern of the solid material. Figure 1C shows representative XRD spectrum for pure Mn₃O₄ and Mn_xO_y nanoaggregate. Hence, we concluded that the solid material recovered at the end of the oxidation reactions formed by

aggregation of mostly Mn₃O₄ nanoparticles along with the other Mn_xO_y derivatives. Additionally, Mn₃O₄ formed in reaction medium was reacted again with H₂O₂ and related olefin was converted to vicinal *cis*-diol while some part of Mn₃O₄ was turned into MnO₂ which is understood by color change from blackish to brown.

FIGURE 1

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

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 has a surface area of 129.6 ± 0.6 m².g⁻¹ the average pore radius of the material was found as 4.6 nm along with the cumulative surface area of pores 117.4 m².g⁻¹ by BJT adsorption analysis (See, FS-1 in ESI). The elemental composition of Mn_xO_y nanoaggregates was determined by EDX analysis. EDX spectra obtained from manganese atom as well as from oxygen, carbon and potassium atom. (See, FS-2 in ESI).

Besides the morphology of the material, we studied its XPS spectra to clarify its chemical composition (Figure 2). The survey XPS spectrum (Figure 2A) of the material indicates the presence of Mn along with the other elements K, Cl, O in which the Cl element might come from the water used in the experiments. The Figure 2B shows the deconvoluted XPS spectrum for Mn2p_{3/2} and Mn2p_{1/2} core-levels at 641.1 eV and 652.8 eV, respectively. The deconvoluted spectra revealed that the material includes the oxidized Mn derivatives and no metallic Mn. The oxide species were found to be mostly Mn₃O₄ and then MnO₂ along with the other possible manganese oxide species with small fractions.¹⁴ This conclusions was also supported by the high-resolution XPS spectrum of Mn3s core-level (Figure 2C) in which the distance of 4.8 eV between the two peaks observed for Mn3s core-level indicates the mainly Mn₃O₄ structure.

FIGURE 2

Figure 2. XPS spectrum of the solid material recovered at the end of oxidation reactions.

Instead of starting with KMnO₄, commercial MnO₂ (sigma-aldrich code No: 63548), Mn₃O₄ (sigma-aldrich code No: 377473) and Mn_xO_y nanoaggregate formed in reaction media were tested in optimized reaction conditions. In these test reactions, the procedure (0°C, N₂ atm.) was applied to cyclohexene (**3**), 3-buten-2-one (**29**) and styrene (**33**) molecules in the presence of commercial MnO₂, Mn₃O₄ and in situ generated Mn_xO_y nanoaggregate. No vicinal *cis*-diols were obtained from the reaction of 10.0 mmol olefin/5.0 mmol MnO₂/30.0 mmol H₂O₂ mixture while corresponding vicinal *cis*-diols were obtained by Mn₃O₄. When we used 30.0 mmol H₂O₂ in this dihydroxylation reaction with together 5.0 mmol Mn₃O₄ and 10.0 mmol olefins (**3**, **29**, **33**), the yields of corresponding vicinal *cis*-diols (**4**, **30**, **34**) were low yields (respectively, 25, 22, 20%). An

amount of olefins were converted to decomposition products, has not been identified. Because of low yields and decomposition of olefins in this test reaction, we used 10.0 mmol H₂O₂, 5.0 mmol Mn₃O₄ and 10.0 mmol olefins and better the yields were obtained about 34% for **4**, 30% for **30**, and 27% for **34** in same reaction condition. When we used 10.0 mmol olefin (**3**, **29**, **33**)/30.0 mmol H₂O₂ mixture and 0.4 g dark brown/blackish solid residue material (Mn_xO_y nanoaggregates) formed in reaction medium, vicinal *cis*-diols (**4**, **30**, **34**) were obtained about 42% for **4**, 40% for **30**, and 36% for **34** in same reaction condition (see methods and Table S2 in the ESI).

In summary, we can conclude that the Mn_xO_y oxide derivatives, mainly Mn₃O₄ nanoaggregates, were in situ generated by KMnO₄/H₂O₂ during the synthesis of vicinal *cis*-diols from olefins. It is thought that Mn₃O₄ formed in reaction medium has a major role in the further oxidation reaction.

Scheme-1 shows the proposed mechanism for the dihydroxylation reaction in aqueous acetone. At the first step of the oxidation reaction, the olefins are oxidized by KMnO₄ in the aqueous acetone and then the expected vicinal *cis*-diols along with Mn_xO_y derivatives are formed. In the second step, oxygen atoms transferred from H₂O₂ to Mn_xO_y residues having as a main component of Mn₃O₄ nanoaggregates.¹⁵ Next, related vicinal *cis*-diols were obtained by ensuring the continuous oxidation of Mn₃O₄ by H₂O₂.

SCHEME 1

Scheme 1. A proposed mechanism for the dihydroxylation of olefins by KMnO₄/H₂O₂ in aqueous acetone.

Table 1 depicts the results of the dihydroxylation of cyclic and linear olefins according to our novel protocol (see ESI for experimental details). The cyclic mono alkenes (**1**, **3**, **5**, **7**, **35**, **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 by high yields about 79-95 %. On the other hand, the molecules bearing dien group (**9**, **11**) were selective for mono-dihydroxylation and corresponding alken-diol compounds (**10**, **12**) were obtained by yield of 60% and 72%, respectively. Methyl-, acetoxy- and epoxy- substituted olefins (**13**, **15**, **17**) were disposed to dihydroxylation reaction in which **15** and **17** were converted to the stereospecific products (**16** and **18**) with the yield of 83% and 65%, respectively. On the other hand, the 4-methyl-1-cyclohexene (**13**) was yielded to syn and anti-isomer products (ratio syn:anti 45:55). Next, Cyclic α,β -unsaturated carbonyl compounds such as cyclopenten-on (**19**) and cyclohexen-on (**22**) were directly converted to corresponding vicinal *cis*-diols (**20** and **22**, respectively, with the 75% and 63% yields). Linear olefins (Table 1, entries 12-17) were easily transformed to respective vicinal *cis*-diols (**24-34**) with good yields (60-76%). The norbornene (**39**) were easily reacted and convert to *exo-cis*-diol **40** in good yield 73%. Some of vicinal *cis*-diols were identified by ¹H- and ¹³C-NMR spectroscopy in comparison with the literature data.⁵

To examine the effect of inert atmosphere on our protocol, we have performed the dihydroxylation of all olefins at 0 °C under N₂ gas. The results revealed that vicinal *cis*-diols were obtained by higher yields than the ones in air. It can be concluded that inert media is more effective for the controlled oxidation of Mn_xO_y derivatives, especially Mn₃O₄ 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. The present KMnO₄/H₂O₂ oxidation system provides many advantages such as being eco-friendly⁶, using fewer equivalents KMnO₄ 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 corresponding vicinal *cis*-diols. On the other hand, we believe that this study will give new insights to material chemists on the synthesis of Mn_xO_y nanoaggregates, mainly Mn₃O₄. In addition to these, lifetime of Mn_xO_y by-products obtained from KMnO₄ can be elongated using various oxidants. By delaying the formation of MnO₂ in this way, functionality of Mn_xO_y by product can be increased.

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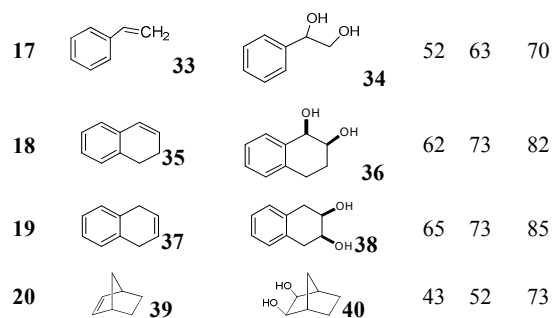
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Table 1. Vicinal *cis*-dihydroxylation of various olefins (10 mmol) by 5.0 mmol. KMnO_4 in the presence of 30.0 mmol H_2O_2 as co-oxidant

Reaction scheme: Olefin + 0.5 eq KMnO_4 , 3 eq H_2O_2 in water:acetone (1:2) yields Vicinal *cis*-diol.

Entry	Olefin	Vicinal <i>cis</i> -diol	Isolated yields		
			(%), 2h	0 °C,	RT 0 °C
1			51	77	82
2			50	78	95
3			67	75	90
4			56	73	79
5			33	47	60
6			58	65	72
7			58	65	72
8			62	75	83
9			31	42	65
10			43	52	75
11			41	50	63
12			47	58	62
13			49	60	66
14			45	54	60
15			60	66	76
16			50	57	68



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 .

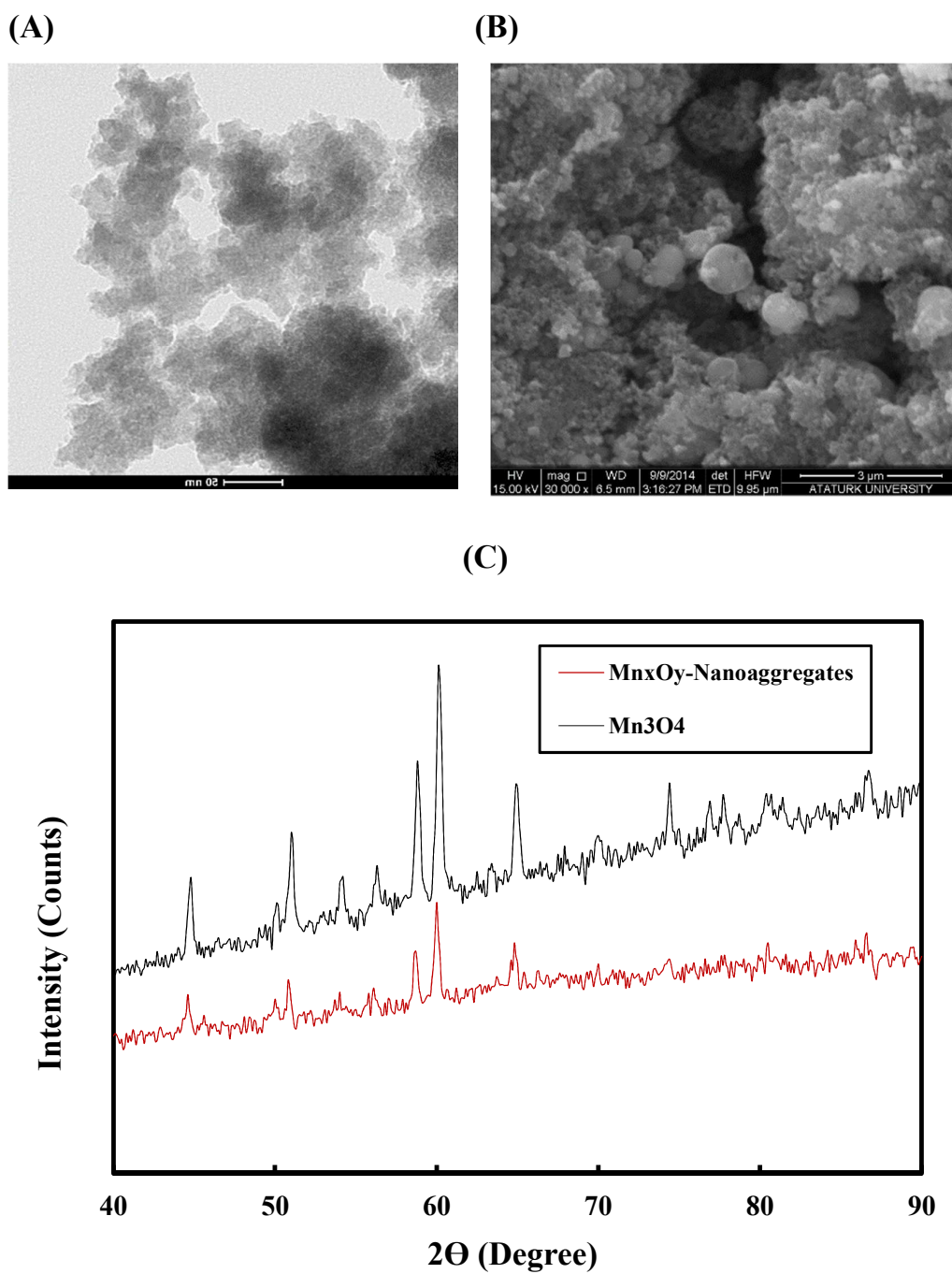


Figure 1. (A) TEM image (B) SEM image (C) XRD pattern spectrum of the solid material recovered at the end of oxidation reactions.

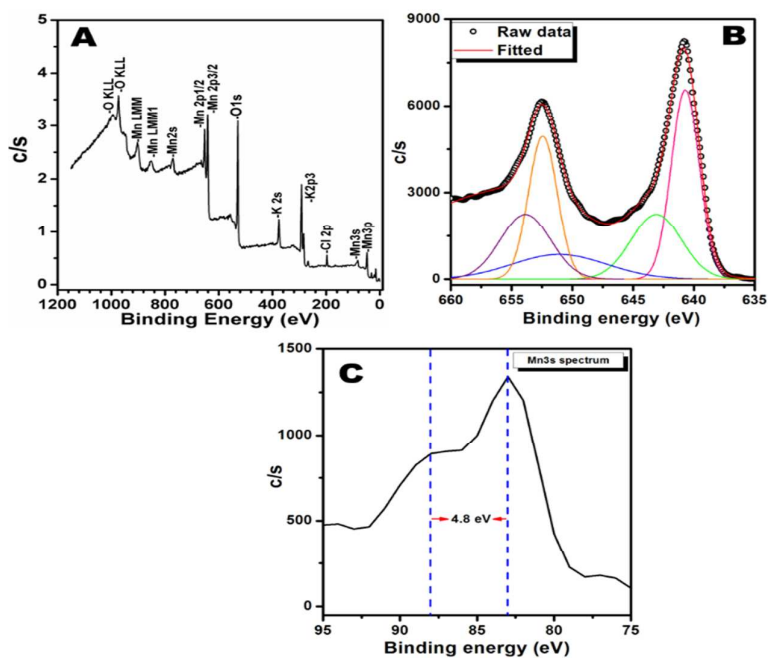
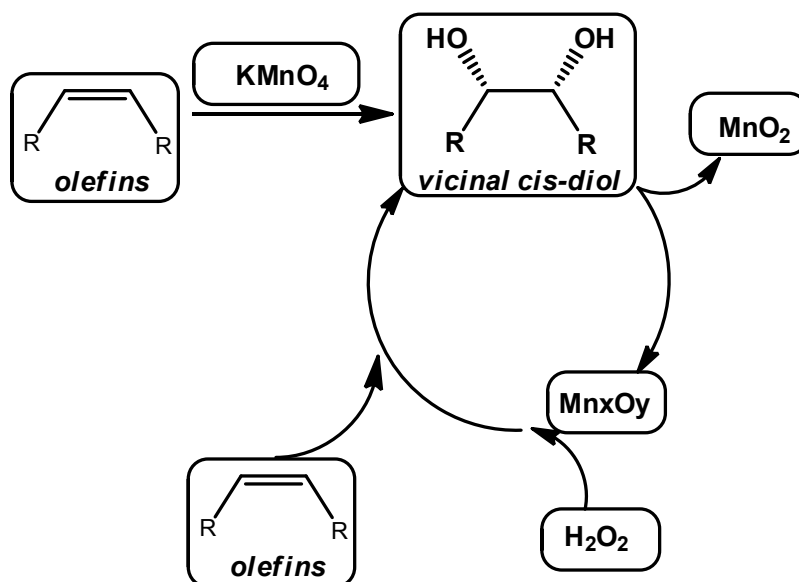


Figure 2. XPS spectrum of the solid material recovered at the end of oxidation reactions.



Scheme 1. A proposed mechanism for the dihydroxylation of 10 mmol olefins by 5 mmol KMnO_4 /30 mmol H_2O_2 in aqueous acetone.