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One-pot synthesis of 1,2/3-triols from the allylic hydroperoxides catalyzed by zeolite-confined osmium(0) nanoclusters

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ABSTRACT

A facile, efficient and eco-friendly method for the one-pot synthesis of 1,2/3-triols from the allylic hydroperoxides were developed by using zeolite-confined osmium(0) nanoclusters as reusable catalyst and without using any co-oxidant (H_2O_2, ^tBuOOH, NMO, etc.) in water/acetone (v/v = 1/4) mixture at room temperature. In this method, the oxygen atom of the allylic hydroperoxide group was transferred to the double bond of the same molecule via zeolite-confined osmium(0) nanoclusters. The method has been successfully applied to various allylic hydroperoxides and the corresponding 1,2/3-triols were obtained in high chemical yield. Moreover, a plausible mechanism was proposed for the catalytic oxidation of allylic hydroperoxide to the respective 1,2/3-triols in the presence of zeolite-Os^0 catalyst gathering all the results collected by testing a variety of allylic hydroperoxides in the presence of zeolite-Os^0 catalyst.

1. Introduction

Cyclitols comprising polyhydroxy groups are important class of compounds found in the plants. The cyclitol derivatives possess some intriguing biological activities to plants such as glycosidase inhibition [1]. The natural and synthetic cyclitol derivatives are widely used in pharmaceutical and food industries owing to their high solubility in water, antibiotic and antioxidant activities [2]. There are also several examples of using cyclitols as organic inhibitor in the corrosion [3] and electrodeposition applications [4]. Hence, the demand on the natural or synthetic cyclitol derivatives has been increasing steadily.

Of cyclitol family, the 1,2,3-triols are indispensable key compounds for the generation of polyhydroxy groups in biomolecules such as carbohydrates, terpenoids and natural sugars [5,6]. The triol moieties provide some important structural features and biological activity to an organic molecule [7]. In addition to their biological and synthetic significance, the triols are used in various industrial processes such as artificial sugar and antibiotic production [8].

There have been many methods proposed for the synthesis of the 1,2,3-triols [5,9]. However, most of these methods have suffered from the use of toxic OsO_4 as the homogenous catalyst and multistep reaction steps. Besides these problems, the formation of some undefined organic-osmium impurities as by-products was generally observed at the end of catalytic reaction [10]. In this regard, a new synthetic method acquiring the simple reaction conditions and elimination of the toxicity of OsO_4 as well as providing high chemical yield and selectivity is required for the synthesis of 1,2,3-triols.

Triols (particularly 1,2,3-triols) **1** are usually prepared by (i) the reduction of keto-diols **2** with $LiAlH_4$ [11] or $NaBH_4$ [12,13], (ii) acid catalyzed ring opening of epoxy alcohols **3** [14], (iii) the substitution of dihydroxy-halogen **4** [15] or (iv) the oxidation of allylic alcohols **5** with OsO_4 [16] or $KMnO_4$ [17] (Scheme 1).

In addition to these methods, our group has recently developed a new protocol for the synthesis of 1,2/3-triols from the allylic hydroperoxides using only the catalytic amount of OsO_4 in the absence of a co-oxidants (Scheme 2) [18]. Our method was successfully applied to many kind of allylic hydroperoxides and the corresponding 1,2/3-triols were obtained in high chemical yields. The key point for our new synthetic method was the role of hydroperoxide groups both as co-oxidant and substrate. It was also the first example for the synthesis of 1,2/3-triols from the allylic hydroperoxides via intramolecular oxygen atom transfer.

In a more recent study, we have also reported an effective and environmentally benign method for the synthesis of 1,2-*cis*-diols from the dihydroxylation of olefins [19]. In this eco-friendly method, the zeolite-confined osmium(0) nanoclusters (zeolite-Os^0) were used as the reusable catalyst and H_2O_2 served as a

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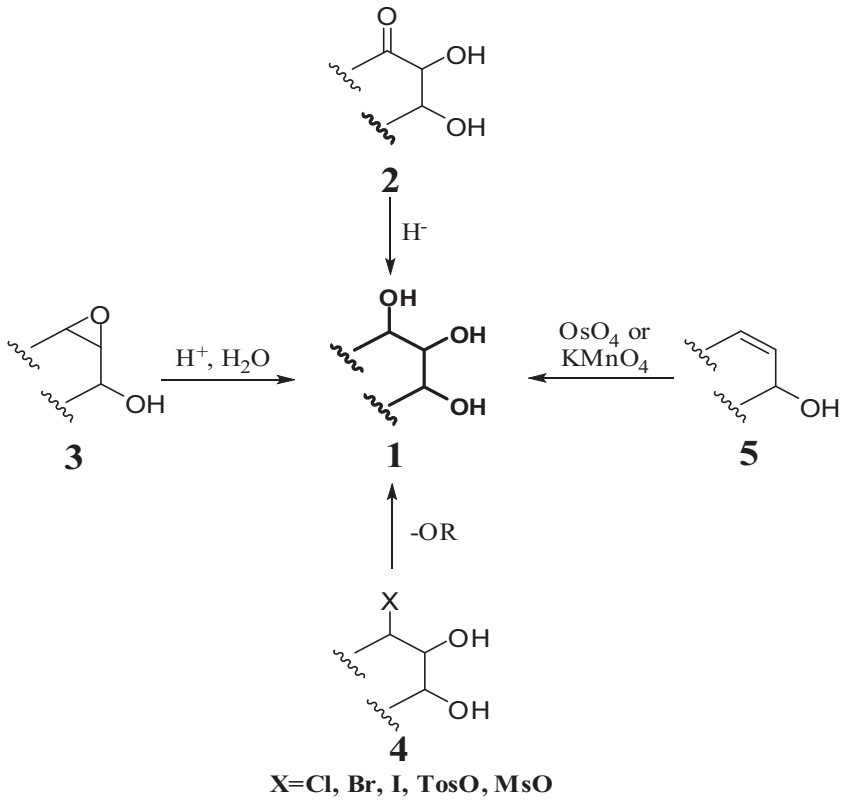
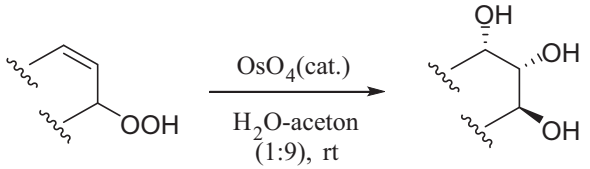


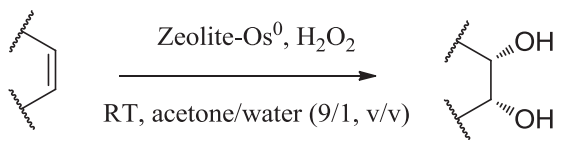
Scheme 1. General methods for the synthesis of 1,2,3-triols.



Scheme 2. The method developed by us for the synthesis of 1,2/3-triols from the allylic hydroperoxides in the presence of catalytic amount of OsO_4 without using any co-oxidant.

co-oxidant in acetone/water (v/v = 9/1) mixture at room temperature (Scheme 3). The catalytic dihydroxylation reaction proceeded smoothly for a wide range olefins and the corresponding 1,2-*cis*-diols were obtained in excellent chemical yield under the optimized conditions.

By combining the latter two methods mentioned above, we developed a facile method for the synthesis of 1,2/3-triols that is presented here. Our effective and eco-friendly method for the one-pot synthesis of 1,2/3-triols involves the zeolite-Os^0 as reusable catalyst and the hydroperoxide group serving as both the co-oxidant and substrate. The use of zeolite-Os^0 catalyst provides not only the elimination of OsO_4 toxicity by recovering it from the reaction solution but also preventing the formation of organic-osmium impurities as by-products. The cyclic or linear allylic hydroperoxides, prepared by the photooxygenation of corresponding alkenes, were successfully converted to the corresponding 1,2/3-triols with the high chemical yields and selectivity. We believe that our new catalytic system for the synthesis of 1,2/3-triols will be a good candidate to be used in the synthetic organic chemistry owing to its effectiveness, simplicity, eco-friendly and reusability.



Scheme 3. The method developed by us for the dihydroxylation of olefins catalyzed by zeolite-Os^0 [19].

2. Experimental

2.1. Materials

Osmium(III) chloride trihydrate ($OsCl_3 \cdot 3H_2O$), sodium borohydride ($NaBH_4$, 98%), zeolite-Y ($Na_{56}[(AlO_2)_{56}(SiO_2)_{140}] \cdot 250H_2O$), 2,3-dimethylbut-2-ene (98%), 2,3-dimethylbut-1-ene (97%), *cis*- or *trans*-but-2-ene (99%), cyclopentene (99%), cyclohexene (99%), cycloheptene (97%), cyclooctene (95%) were purchased from Sigma–Aldrich® and were used without further purification. Other organic compounds; octalin (96%), 1,4-dihydronaphthalene (98%), 7-oxabicyclo[4.1.0]hept-3-ene (98%) synthesized by the established methods in the literature. Deionized water was distilled by water purification system (Milli-Q system). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C. Transmission electron microscope images were obtained by a JEOL 2100 TEM (200 kV). ^1H and ^{13}C NMR spectra were recorded on a Varian 200 MHz or Bruker Avance DPX 400 MHz spectrometer.

2.2. General procedure for the preparation of zeolite-confined osmium(0) nanoclusters

The zeolite-Os^0 catalysts were prepared by using our reported procedure including the ion-exchange of Os^{3+} ions with the extra

framework Na^+ ions of zeolite-Y and then following reduction of the Os^{3+} ions in solution and well-characterized by using various advanced techniques [19,20].

2.3. General procedure for the synthesis of the allylic hydroperoxides

The 10 mmol of alkene was dissolved in CH_2Cl_2 containing TPP (5–10 mg) in a jacketed glass balloon and irradiated using tungsten lamb (500 W) with air bubbling (oxygen gas) at room temperature. The photooxygenation reaction was monitored by TLC. The most of the reactions completed over the time period of 8–24 h. The solvent (CH_2Cl_2) was evaporated at 20 °C and 20 mmHg at the end of the reaction. The residue was separated by (silica gel) thin layered chromatography (TLC) with hexane:ethylene chloride. The ratio and yields were calculated by ^1H NMR spectra.

2.4. General procedure for the synthesis of the 1,2/3-triols

In a typical synthesis of the 1,2/3-triols, 10 mmol of allylic hydroperoxide was dissolved in the H_2O/acetone (v/v: 1:4) mixture at room temperature. Next, a zeolite-confined osmium(0) nanoclusters catalyst (100 mg, 0.01 mmol Os) was added into the allylic hydroperoxide solution at room temperature. Reaction was then continued under vigorous stirring at room temperature. The progress of the catalytic reaction was monitored by thin layered chromatography (TLC). The most of the reactions completed over the time period of 48–62 h (Table 1). After the completion of the reaction, the zeolite-Os^0 catalysts were removed by centrifugation at 7000 rpm and washed several times with acetone/water mixture. Then, the catalysts were allowed to dry for the further use. The supernatant was removed by using a rotary evaporator. Finally, the crude residue was directly purified by column chromatography on silica gel using EtOAc–hexanes as the eluent to separate the synthesized 1,2/3-triols. The yields of the 1,2/3-triols were determined by ^1H and ^{13}C NMR spectra which taken in D_2O or $CDCl_3$ (Table 1).

2.5. Spectral data (^1H NMR, ^{13}C NMR and FTIR) for the synthesized 1,2/3-triols

rac-3-hydroperoxy-2,3-dimethylbut-1-ene (***1a***): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.07 (bs, 1 H), 4.95–4.89 (m, 2 H), 1.77 (s, 3 H), 1.32 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 148.3, 112.0, 84.4, 28.8, 24.8, 24.1, 18.9. IR (KBr, cm^{-1}): 3392.6, 2984.4, 1452.3, 1374.8, 1149.8, 900.1.

rac-2,3-dimethylbutane-1,2,3-triol (***1b***): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.89 (d, 1 H, J = 11.5 Hz), 3.48 (d, 1 H, J = 11.5 Hz), 1.26 (s, 3 H), 1.23 (s, 3 H), 1.06 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 76.5, 75.5, 68.6, 25.5, 24.9, 20.4. IR (KBr, cm^{-1}): 3390.9, 2980.6, 1381.8, 1041.3.

rac-2-(hydroperoxymethyl)-3-methylbut-1-ene (***2a***): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.02 (bs, 1 H), 5.06 (d, 1 H, J = 7.3 Hz), 4.50 (s, 1 H), 2.40 (hept., 1 H, J = 6.9 Hz), 1.07 (d, 1 H, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 150.3, 112.5, 79.5, 31.5, 21.7. IR (KBr, cm^{-1}): 3500.2, 2918.76, 1566.7, 1359.44, 1149.8, 995.8.

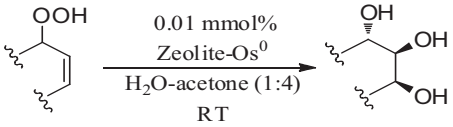
rac-2-isopropylpropane-1,2,3-triol (***2b***): ^1H NMR (400 MHz, D_2O, ppm): δ = 3.47 (s, 4 H), 1.83–1.76 (m, 1H), 0.80 (d, 6 H, J = 7.0 Hz). ^{13}C NMR (100 MHz, D_2O, ppm) δ = 75.0, 63.1, 30.1, 15.7. IR (KBr, cm^{-1}): 3114.8, 2863.3, 1443.3, 1057.3.

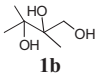
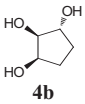
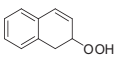
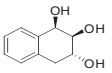
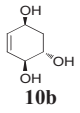
rac-3-hydroperoxybut-1-ene (***3a***): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.98 (bs, 1 H), 5.84 (ddd, 1 H, J = 17.4, 10.4, 7.2 Hz), 5.30 (m, 2 H), 4.50 (p, 1 H, J = 6.5 Hz), 1.27 (d, 3 H, J = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.8, 118.3, 82.7, 18.0. IR (KBr, cm^{-1}): 3702.0, 2991.6, 1524.5, 1318.4, 1170.9, 966.8.

rac-butane-1,2,3-triol (***3b***): ^1H NMR (400 MHz, D_2O, ppm): δ = 3.70–3.64 (m, 1H), 3.60–3.54 (m, 1H), 3.48–3.38 (m, 2H), 1.10 (d, 3H, J = 6.4 Hz). ^{13}C NMR (100 MHz, D_2O, ppm) δ = 75.8, 67.9, 62.6, 17.4. IR (KBr, cm^{-1}): 3708.2, 2991.6, 1494.7, 1187.9.

rac-3-hydroperoxycyclopent-1-ene (***4a***): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.58 (bs, 1H), 6.13 (m, 1 H), 5.79 (m, 1 H), 5.12 (m, 1 H), 2.51–1.90 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 139.5, 128.2, 91.13, 31.4, 28.1. IR (KBr, cm^{-1}): 3366.8, 2934.5, 1614.6, 1359.4, 1038.4, 954.5.

Table 1
The synthesized 1/2,3-triols from the allylic hydroperoxides in the presence of zeolite-Os^0 catalyst in water/acetone (v/v: 1/4) mixture at room temperature.[a]



Entry	Substrate	Product	Yield %[b]	Time (h)
1	 **1a**	 **1b**	83	48
2	 **2a**	 **2b**	87	40
3	 **3a**	 **3b**	85	44
4	 **4a**	 **4b**	91	56
5	 **5a**	 **5b**	93	58
6	 **6a**	 **6b**	87	60
7	 **7a**	 **7b**	75	60
8	 **8a**	 **8b**	88	36
9	 **9a**	 **9b**	58	62
10	 **10a**	 **10b**  **10c**	92 8	56

[a] All reactions were performed in aqueous acetone mixture (10.0 mL, acetone/water = 4/1, v/v) using zeolite-Os^0 catalyst (100.0 mg, 2.1 wt% Os), allylic hydroperoxide (10 mmol), at room temperature. All the 1,2/3-triols were also characterized after their transformation into corresponding acetates.
[b] Isolated yield.

rac-cyclopentane-1,2/3-triol (***4b***): ^{1}H NMR (400 MHz, D_2O, ppm): δ = 3.98–3.95 (m, 2 H), 3.64 (m, 1 H), 1.99–1.85 (m, 2 H), 1.43–1.23 (m, 2 H). ^{13}C NMR (100 MHz, D_2O, ppm): δ = 78.9, 75.7, 71.7, 28.4, 27.7. IR (KBr, cm^{-1}): 3366.9, 2938.1, 1569.1, 1410.5.

rac-3-hydroperoxycyclohex-1-ene (***5a***): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.03 (bs, 1 H), 5.94 (m, 1 H), 5.69 (m, 1 H), 4.43 (m, 1 H), 2.05–1.47 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 134.4, 124.3, 78.6, 26.5, 25.4, 18.5. IR (KBr, cm^{-1}): 3366.4, 2934.3, 1650.6, 1392.5, 1066.3, 944.8.

rac-cyclohexane-1,2/3-triol (***5b***): ^{1}H NMR (400 MHz, D_2O, ppm): δ = 3.96 (m, 1 H), 3.73 (m, 1 H), 3.33 (m, 1 H), 1.89–1.23 (m, 6 H). ^{13}C NMR (100 MHz, D_2O, ppm): δ = 76.0, 71.0, 69.9, 31.6, 30.4, 18.3. IR (KBr, cm^{-1}): 3366.7, 2937.8, 1574.2, 1069.4.

rac-3-hydroperoxycyclohept-1-ene (***6a***): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.21 (bs, 1 H), 5.79–5.71 (m, 2 H), 4.57 (m, 1 H), 2.14–1.31 (m, 8 H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ = 132.7, 132.6, 85.3, 30.9, 28.6, 26.8, 26.6. IR (KBr, cm^{-1}): 3374.8, 2928.3, 1651.9, 1446.7, 1003.6, 835.6.

rac-cycloheptane-1,2/3-triol (***6b***): ^{1}H NMR (400 MHz, D_2O, ppm): δ = 3.82 (m, 1 H), 3.54 (m, 1 H), 3.47 (dd, 1 H, J = 7.0, 2.6 Hz), 1.62–1.28 (m, 8 H). ^{13}C NMR (100 MHz, D_2O, ppm): 78.7, 73.9, 71.9, 32.1, 29.5, 23.3, 22.7. IR (KBr, cm^{-1}): 3398.9, 2924.4, 1654.6, 1377.9.

rac-3-hydroperoxycyclooct-1-ene (***7a***): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.55 (bs, 1 H), 5.72 (m, 1 H), 5.63 (m, 1 H), 4.93 (m, 1 H), 2.22–1.32 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 131.6, 130.7, 83.5, 33.0, 29.0, 26.6, 26.3, 23.6. IR (KBr, cm^{-1}): 3390.6, 2928.9, 1653.8, 1451.1, 1040.2, 754.3.

rac-cyclooctane-1,2/3-triol (***7b***): ^{1}H NMR (400 MHz, D_2O, ppm): δ = 3.87 (m, 1 H), 3.64 (m, 1 H), 3.51 (m, 1 H), 1.58–1.24 (m, 10 H). ^{13}C NMR (100 MHz, D_2O, ppm): 78.0, 72.9, 70.5, 32.3, 30.2, 25.9, 25.4, 22.6. IR (KBr, cm^{-1}): 3434.8, 2528.2, 1645.6, 1434.7.

rac-4a-hydroperoxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (***8a***): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.60 (bs, 1 H), 5.68 (dd, 1 H, J = 4.8, 2.6 Hz), 2.31–1.20 (m, 14 H). ^{13}C NMR (100 MHz, $CDCl_3$ $CDCl_3$, ppm) δ = 136.3, 127.4, 81.4, 35.3, 32.5, 32.3, 27.5, 25.8, 21.6, 18.9. IR (KBr, cm^{-1}): 3109.2, 2868.3, 1560.8, 1384.6, 1245.7, 903.5.

rac-decahydronaphthalene-1,4a,8a-triol (***8b***): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.92 (dd, 1 H, J = 10.0, 4.8 Hz), 2.12–1.06 (m, 14 H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 78.4, 75.1, 70.9, 42.5, 30.1, 27.5, 27.0, 26.1, 20.0, 18.1. IR (KBr, cm^{-1}): 3550.2, 2929.9, 1568.4, 1169.2.

rac-2-hydroperoxy-1,2-dihydronaphthalene (***9a***): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.26–7.08 (m, 4 H), 6.73 (d, 1 H, J = 9.6 Hz), 6.04 (dd, 1 H, J = 9.6, 4.8 Hz), 4.81 (m, 1 H), 3.35 (dd, 1 H, J = 17.2, 4.8 Hz), 3.03 (dd, 1 H, J = 17.2, 6.05 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 133.7, 133.1, 132.4, 128.6, 128.3, 127.3, 127.0, 123.2, 77.3, 31.8. IR (KBr, cm^{-1}): 3390.8, 3042.0, 1634.3, 1488.1, 1451.7, 997.4, 786.1.

rac-1,2,3,4-tetrahydronaphthalene-1,2/3-triol (***9b***): ^{1}H NMR (400 MHz, D_2O, ppm): δ = 7.33–7.18 (m, 4 H), 4.63 (m, 1 H), 4.01 (m, 1 H), 3.59 (m, 1 H)), 3.05–2.52 (m, 2 H). ^{13}C NMR (100 MHz, D_2O, ppm): 138.5, 137.3, 130.3, 129.7, 128.9, 128.5, 76.5, 72.8, 68.9, 38.9. IR (KBr, cm^{-1}): 3502.4, 3008.4, 1733.6, 1370.0, 1229.5, 1016.4.

rac-3-hydroperoxy-7-oxabicyclo[4.1.0]hept-4-ene (***10a***): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.09 (bs, 1 H), 6.13 (ddd, 1 H, J = 10.2, 5.2, 1.8 Hz), 6.03 (dd, 1 H, J = 10.2, 1.9 Hz), 4.58 (m, 1 H), 3.53 (m, 1 H), 3.31 (m, 1 H), 2.58 (ddd, 1 H, J = 14.1, 7.8, 2.4 Hz), 1.43 (ddd, 1 H, J = 14.1, 10.2, 1.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 135.5, 126.5, 78.6, 53.6, 49.1, 27.3. IR (KBr, cm^{-1}): 3366.6, 2934.3, 1650.7, 1600.8, 1430.9, 1392.5, 944.8.

rac-cyclohex-5-ene-1,2,4-triol (***10b***): ^{1}H NMR (400 MHz, D_2O, ppm): δ = 5.75 (d, 1 H, J = 10.5 Hz), 5.66 (dd, 1 H, J = 10.5, 1.8 Hz), 4.28 (q, 1 H, J = 3.8 Hz), 3.91 (ddd, 1 H, J = 7.2, 1.7, 1.4 Hz), 3.73 (ddd, J = 1 H 11.9, 7.2, 4.7 Hz), 1.82 (m, 2 H). ^{13}C NMR (100 MHz, D_2O, ppm): 133.8, 132.3, 74.3, 71.4, 67.1, 38.7. IR (KBr, cm^{-1}): 3387.2, 3080.6, 2953.3, 2927.1, 2876.9, 1676.4, 1625.5, 1446.7, 1242.7, 1217.9, 1063.0, 1038.1.

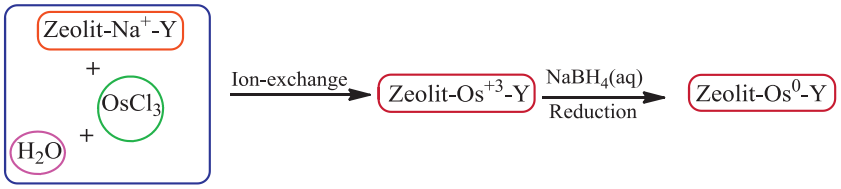
rac-7-oxabicyclo[4.1.0]heptane-2,3,4-triol (***10c***): ^{1}H NMR (400 MHz, D_2O, ppm): δ = 3.83–3.78 (m, 2 H), 3.58 (q, 1 H, J = 5.8 Hz), 3.41 (m, 1 H), 3.08 (m, 1 H)), 2.21 (d, 1 H, J = 5.8 Hz), 1.91 (ddd, 1 H, J = 14.7, 10.1, 2.2 Hz). ^{13}C NMR (100 MHz, D_2O, ppm): 70.0, 67.6, 64.9, 55.2, 54.9, 26.5. IR (KBr, cm^{-1}): 2931.5, 1367.1, 1223.3, 1034.9.

3. Results and discussion

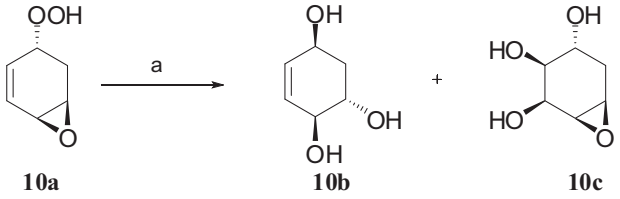
The zeolite-Os^0 catalyst was prepared by using our established procedure and characterized by using many advanced techniques [20]. In a typical procedure for the synthesis of zeolite-Os^0, ion-exchange of Os^{3+} ions with the Na^+ ions of zeolite-Y took place and then followed by the reduction of Os^{3+} ions within the cages of zeolite with excess $NaBH_4$ in aqueous solution. The cation sites left by Os^{3+} ions upon reduction are re-occupied by the sodium cations coming from sodium borohydride (Scheme 4). The Os content of zeolite-Os^0 catalyst was determined by the inductively coupled plasma optical emission spectroscopy (ICP-OES) as 2.1 wt% that is used for the calculation of Os loading in all the catalytic reactions.

Table 1 gives the list of cyclic or linear allylic hydroperoxides, which were prepared by photooxygenation of the corresponding alkenes according to our reported procedure [18], and used in the catalytic synthesis of 1,2/3-triols as both the substrate and co-oxidant. All of the allylic hydroperoxides were identified by ^{1}H and ^{13}C NMR spectroscopy in comparison with the literature data. All of the allylic hydroperoxides given in Table 1 were reacted in acetone/water (v/v = 4/1) mixture at room temperature in the presence of zeolite-Os^0 catalyst and without using any co-oxidant (H_2O_2, ^{t}BuOOH, NMO, etc.). The products of the catalytic reactions were characterized by ^{1}H and ^{13}C NMR spectroscopy. The analysis of the NMR spectra taken after the catalytic reactions shows that both the cyclic or linear allylic hydroperoxides were successfully converted to the corresponding 1,2/3-triols with the high chemical yields and selectivity (Table 1, entries 1–11). For example, the linear allylic hydroperoxides, rac-3-hydroperoxy-2,3-dimethylbut-1-ene (**1a**), rac-2-(hydroperoxymethyl)-3-methylbut-1-ene (**2a**), and rac-3-hydroperoxybut-1-ene (**3a**) were converted to the rac-2,3-dimethylbutane-1,2,3-triol (**1b**) (83%), rac-2-isopropylpropane-1,2,3-triol (**2b**) (87%) and rac-butane-1,2,3-triol (**3b**) (85%), respectively (Table 1, entries 1–3). The cyclic allylic hydroperoxides: the rac-3-hydro peroxycyclopent-1-ene (**4a**), 3-rac-hydroperoxy-cyclo-hex-1-ene (**5a**), rac-3-hydroperoxycyclo hept-1-ene (**6a**) and (Z)-rac-3-hydroperoxy-cyclooct-1-ene (**7a**) were yielded to the rac-cyclopentane-1,2/3-triol (**4b**) (91%), rac-cyclohexane-1,2/3-triol (**5b**) (93%), rac-cycloheptane-1,2/3-triol (**6b**) (87%), and rac-cyclooctane-1,2/3-triol (**7b**) (75%), respectively (Table 1, entries 4–7).

On the other hand, the bicyclic allylic hydroperoxides were also studied under the same reaction conditions. In the presence of zeolite-Os^0 rac-4a-hydroperoxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (**8a**) and *rac*-2-hydroperoxy-1,2-dihydronaphthalane (**9a**) gave the expected products of rac-decahydro naphthalene-1,4a,8a-triol (**8b**) (88%) and *rac*-2,3-dihydroxy-1,2,3,4-tetrahydronaphthalen-1,2/3-triol (**9b**) (58%), respectively (Table 1, entries 8 and 9). Different from the others, the *rac*-3-hydroperoxy-7-oxabicyclo[4.1.0]hept-4-ene (**10a**) was converted to *rac*-cyclohex-5-ene-1,2,4-triol (**10b**) and *rac*-7-oxabicyclo[4.1.0]heptane-2,3,4-triol (**10c**) with the yield of 92% and 8%, respectively in the presence of zeolite-Os^0 catalyst (Scheme 5).



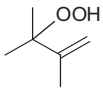
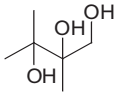
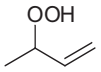
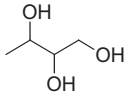
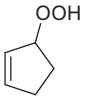
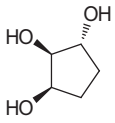
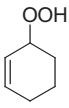
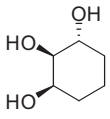
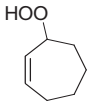
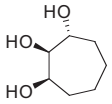
Scheme 4. A representative cartoon for the synthesis of zeolite-confined osmium(0) nanoclusters (zeolite-Os^0).



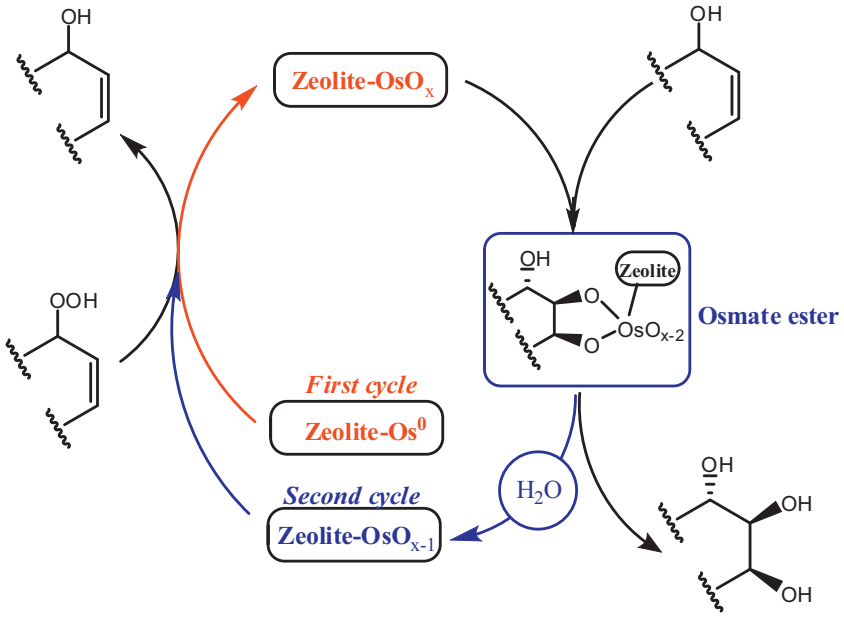
Scheme 5. Oxidation of rac-3-hydroperoxy-7-oxabicyclo[4.1.0]hept-4-ene (**10a**) in the presence of zeolite-Os^0. Reagent and conditions: (a) 0.01 mmol% zeolite-Os^0, H_2O:acetone (1:4), 56 h, rt., ratios of products **10b**/**10c** = 11.5:1.

A plausible mechanism could be proposed for the catalytic oxidation of allylic hydroperoxide to the respective 1,2/3-triols in the presence of zeolite-Os^0 catalyst gathering all the results collected by testing a variety of allylic hydroperoxides. The proposed mechanism is shown in Scheme 6. At the first step of the catalytic reaction (first cycle), the Os(0) nanosclusters within the zeolite framework are oxidized to zeolite-OsO_x by the allylic hydroperoxides in the aqueous acetone and the expected allylic alcohol is formed. In the second step, two oxygen atoms transferred from the zeolite-OsO_x to allylic alcohol via the osmate ester formation and the zeolite-OsO_{x-2} is formed. Next, the zeolite-OsO_{x-2} in osmate ester is transformed to zeolite-OsO_{x-1} after its reaction with water in the reaction media and thus the first cycle is completed. The second cycle of the mechanism starts with the OsO_{x-1} and the other parts of the mechanism follow the same way as described in the first cycle. It is assumed that all of these reaction steps in the proposed mechanism occur within the zeolite-Y framework. It is noteworthy to mention that all the catalytic reactions were performed in the

Table 2
The five-run reusability test for the zeolite-Os^0 catalysts in synthesis of 1,2/3-triols from the allylic hyroperoxides.[a]

Entry	Substrate	Product	Yield % 1st run	Yield % 5th run
1			83	80
2			85	82
3			91	90
4			93	90
5			87	82

[a] All reactions were performed in aqueous acetone mixture (10.0 mL, acetone/water = 4/1, v/v) using 100.0 mg zeolite-Os^0 (2.1 wt% Os), 10 mmol of allylic hydroperoxide (5 times) at room temperature.



Scheme 6. The proposed mechanism for the synthesis of 1,2/3-triols from the allylic hydroperoxides in the presence of zeolite-Os^0 catalyst.

aqueous acetone because of the solubility of allylic hydroperoxides in acetone and the important role of water in the mechanism.

The zeolite-Os^0 catalyst was recovered from the reaction solution by simple centrifugation and re-used for five times in the 1,2/3-triols synthesis from various allylic hydroperoxides (Table 2, entries 1–5). As clearly seen from Table 2, there is no important loss in the chemical yield (the loss in the chemical yields is in the rage of 2–5%) of the corresponding 1,2/3-triols from the allylic hydroperoxides in the presence of zeolite-Os^0 catalysts even after 5th catalytic runs. The ICP-OES analyses performed on the catalytic reaction solutions showed that the negligible amount of osmium was detected (<1 ppm), which is a clear evidence for no leaching of osmium into the reaction solution. In this regard, we believed that the small decrease in the chemical yields of 1,2/3-triols during the five cycles reusability test most probably stems from loss of some of zeolite-Os^0 catalyst during the centrifugation and drying process.

4. Conclusions

In conclusion, we have reported a facile and eco-friendly catalytic system for the one-pot synthesis of various 1,2/3-triols from the allylic hydroperoxides. Zeolite-confined osmium(0) nanoclusters were used as the reusable catalyst and exhibited excellent activity in the synthesis of 1,2/3-triols from the allylic hydroperoxides in the absence of a co-oxidant. The novel methodology presented here provides many advantages over the existed methods for the synthesis of 1,2/3-triols such as providing one-pot synthesis without using any co-oxidants, being eco-friendly owing to the elimination of OsO_4 toxicity and being economical due to the recovery of the zeolite-Os^0 catalysts. We hope that the method described here will open a new perspective for the synthetic organic chemists on the synthesis of cyclitols derivatives for different applications.

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