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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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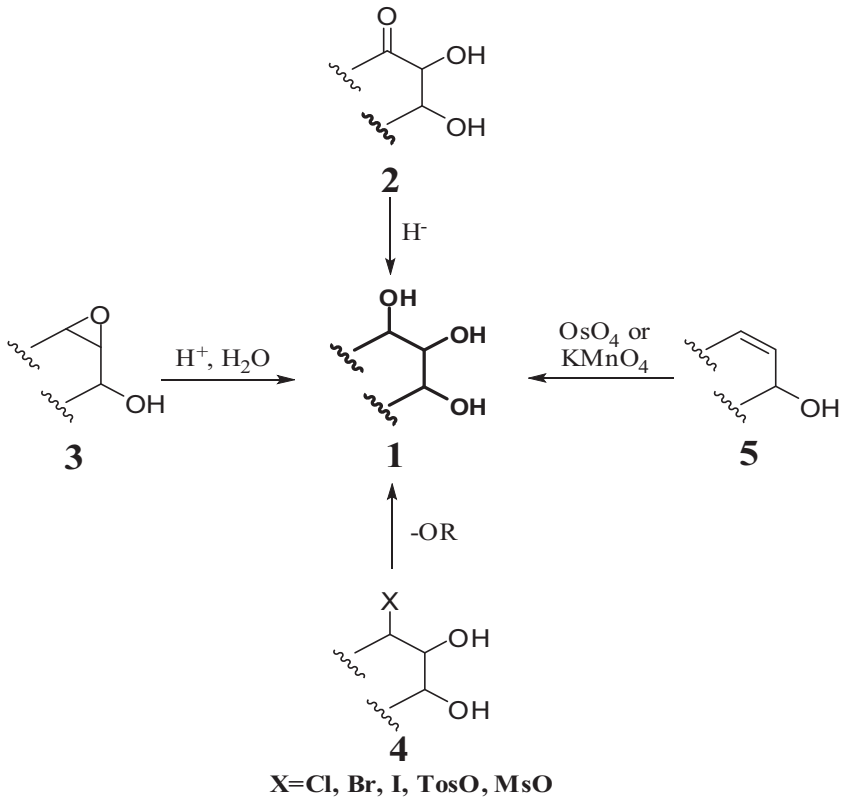
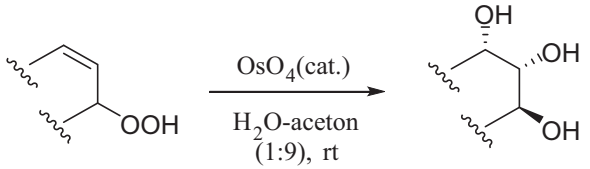


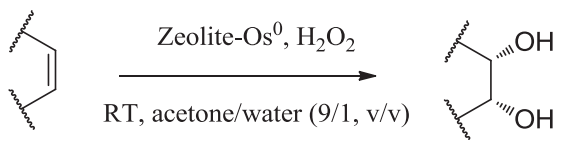
Scheme 1. General methods for the synthesis of 1,2,3-triols.



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