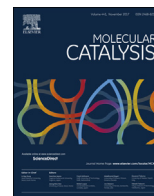




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Heteropoly acid catalysts for the valorization of biorenewables: Isomerization of caryophyllene oxide in green solvents

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ABSTRACT

The isomerization of caryophyllene oxide, one of the most widespread sesquiterpenes found in various essential oils, is catalyzed by the acidic Cs salt of tungstophosphoric heteropoly acid, Cs_{2.5}H_{0.5}PW₁₂O₄₀, to give rare polycyclic oxygenated sesquiterpenes with a clovane structure. Cloven-9-ol and clovan-2,9-diol can be obtained with up to 80% combined selectivity and 60% individual selectivity each (under different reaction conditions), which is the best result reported for these compounds so far. The process is environmentally benign and can be performed not only in conventional solvents such as 1,2-dichloroethane and acetone but also in eco-friendly "green" organic solvents such as dimethylcarbonate, diethylcarbonate and 2-methyltetrahydrofuran. The reactions occur under ambient conditions at low catalyst loadings without catalyst leaching. The solid catalyst can be simply centrifuged from the reaction mixture, and low boiling solvents can be separated from reaction products by distillation.

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1. Introduction

Terpenes are found in nature in essential oils of plant materials, often as main constituents. Natural terpenes and their synthetic derivatives are very important for perfumery, pharmaceutical and cosmetics industries [1–3]. In particular, many value-added terpenoids are industrially produced through the acid catalyzed transformations of more abundant terpenes [1–3]. In most of these syntheses, large amounts of hazardous mineral acids are still used as homogeneous catalysts, which results in serious pollution and corrosion problems. The development of sustainable and environmentally benign processes based on the application of solid acid catalysts is very important for terpene chemistry as it allows for extending the commercial use of easily affordable and bio-renewable essential oils.

Heteropoly acids (HPAs) of the Keggin series, such as H₃PW₁₂O₄₀ (HPW), are widely recognized as attractive and green acid catalysts for many important processes in fine chemistry [4–6]. Due to the strong Brønsted acidity and high chemical stability,

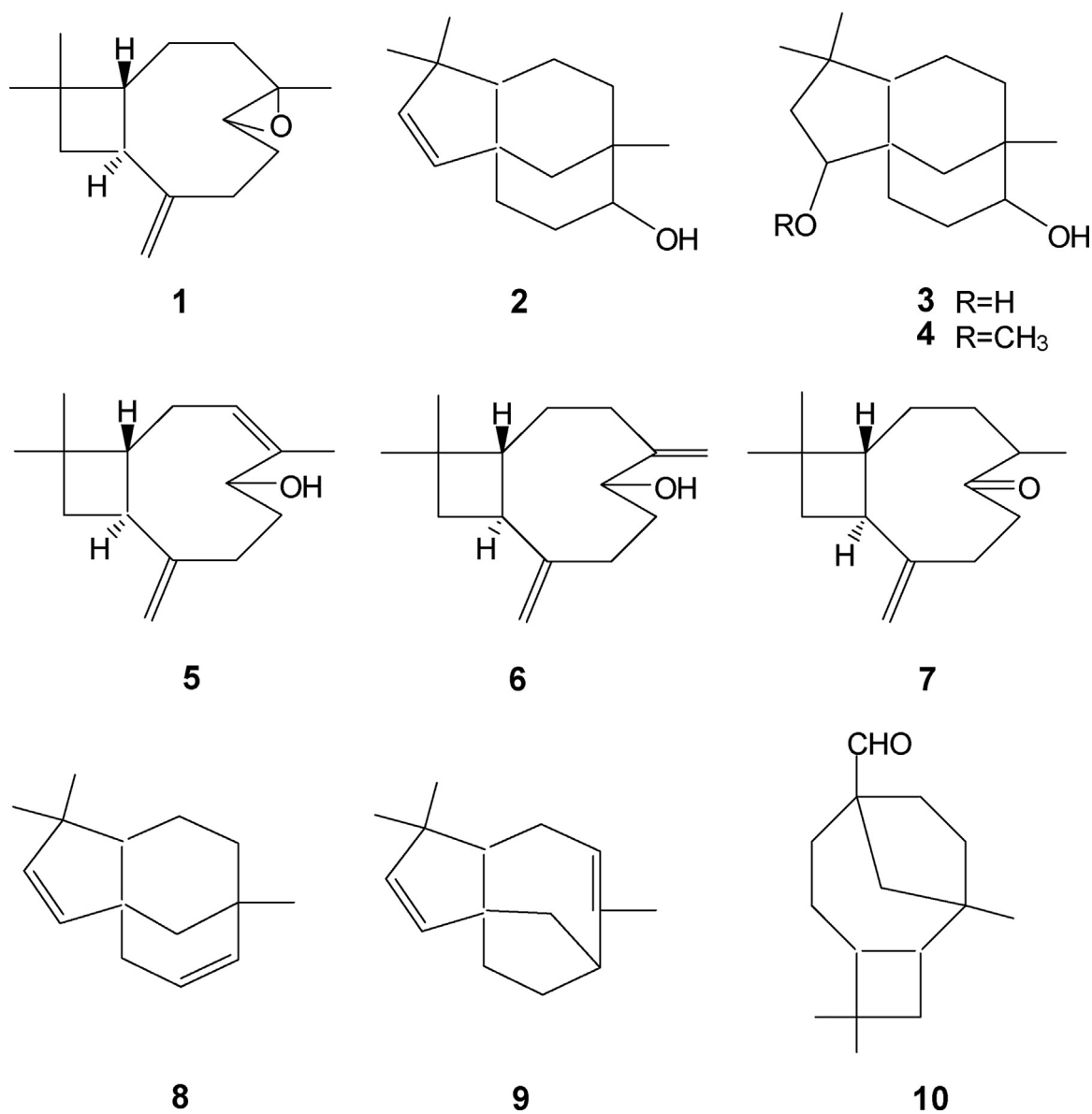
HPAs usually show better catalytic performance than traditional acid catalysts, e.g. mineral acids, zeolites and clays. Supported HPAs can be used as heterogeneous catalysts in non-polar and weakly polar media without leaching problems. On the other hand, for heterogeneous catalysis in polar solvents, where HPAs are highly soluble, their insoluble acidic salts represent excellent alternatives [7–10]. In particular, several examples of successful use of Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW), a compound with strong Brønsted acidity and large surface area, as a heterogeneous acid catalyst have been reported [11–16].

Caryophyllene oxide (**1**), one of the most widespread sesquiterpenes, is found in various essential oils, such as clove or lavender oils [17,18] (Scheme 1). Caryophyllene oxide can also be obtained synthetically by the epoxidation of β-caryophyllene, the main hydrocarbon component of clove and copaiba oils [17–19]. Due to the recognized biological activity of caryophyllane compounds, the copaiba oil is traditionally used in popular medicine and plays an important role in the Brazilian export of pharmaceutical products [19]. Caryophyllane derivatives are also widely used as aromatic ingredients (woody, floral, fruity) in perfumes, food and tobacco products [2,18].

Caryophyllene and its derivatives have an unusual structure with a cyclobutane ring fused in a *trans* manner with a nine-

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Scheme 1. Possible products of the acid-catalyzed transformation of caryophyllene oxide (1).

membered ring (Scheme 1). The skeletal rearrangements of these compounds could provide access to rarer sesquiterpenoids, for example, to the compounds with caryolane and clovane tricyclic structures [17]. However, the development of selective reactions involving caryophyllenic substrates is a highly challenging task as these strained molecules undergo a variety of transformations with a remarkable facility. Probably for this reason, the reports on selective catalytic reactions of caryophyllanes are scarce in the literature. In particular, it has been reported that the acid-promoted transformations of caryophyllene oxide usually result in a complex mixture of polycyclic products due to *trans*-annulation reactions [20–25]. Some of these products are shown in Scheme 1. Only few reports described reasonable selectivities for individual products (usually less than 30–40%). In most of those works hazardous homogeneous catalysts or large over-stoichiometric amounts of solid acids were used to promote the transformations of caryophyllene oxide. For example, diol **3** was detected as a preferential product in acetone solutions of sulfuric acid [20,25]. Allylic alcohols **5** and **6** were major products formed from caryophyllene oxide in acetone or DMSO solutions in the presence of highly toxic tetracyanoethylene as the

catalyst [23]. The formation of ketone **7** as a major product was detected at the isomerization of caryophyllene oxide in toluene solutions over FeSO₄ or Zr(SO₄)₂ [21]. The reaction over sulfated silica gave mainly dienes **8** and **9**, whereas the reaction over sulfated alumina gave allylic alcohol **6** or aldehyde **10** depending on the conditions applied [25].

For several years we have concentrated our efforts on the catalytic transformation of terpenic compounds, in particular, acid catalyzed transformations. As a result, we have reported several successful applications of heteropoly acid catalysts in liquid-phase reactions, such as isomerization [14,26,27], esterification/etherification [16,28,29] and cycloaddition [15,30]. In the present work, we investigate the silica-supported HPW and its Cs salt, CsPW, as heterogeneous catalysts for the isomerization of caryophyllene oxide. These reactions are performed in various liquid media, including environmentally friendly non-toxic organic solvents (so-called ‘green’ solvents) such as dimethylcarbonate (DMC), diethylcarbonate (DEC) and 2-methyltetrahydrofuran (MeTHF). To our knowledge, no attempt to use HPA catalysts for this reaction has been made before. Moreover, as far as we know,

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