

Heteropoly acid catalysts in upgrading of biorenewables: cycloaddition of aldehydes to monoterpenes in green solvents

Rafaela F. Cotta ^a, Kelly A. da Silva Rocha ^b, Elena F. Kozhevnikova ^c, Ivan V. Kozhevnikov ^c and Elena V. Gusevskaya ^{a,*}

^a*Departamento de Química, Universidade Federal de Minas Gerais, 31270-901, Belo Horizonte, MG, Brazil*

^b*Departamento de Química, Universidade Federal de Ouro Preto, 35400-000, Ouro Preto, MG, Brazil*

^c*Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK*

Abstract

Acidic Cs salt of tungstophosphoric heteropoly acid, Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW), is excellent solid acid catalyst for liquid-phase cycloaddition reactions of biomass-based and easily available from essential oils monoterpene compounds, such as limonene, α -terpineol, α -pinene, β -pinene and nerol, with aldehydes, including benzaldehyde, crotonaldehyde as well as biomass-derived cuminaldehyde and *trans*-cinnamaldehyde. The reactions give oxabicyclo[3.3.1]nonene compounds potentially useful for the fragrance and pharmaceutical industries in good to excellent yields. The process is environmentally benign and can be performed in eco-friendly “green” organic solvents such as dimethylcarbonate, diethylcarbonate and 2-methyltetrahydrofuran under mild conditions at low catalyst loadings without leaching problems. The solid CsPW catalyst can be easily separated from the reaction media and low-boiling solvents can be removed by distillation. Silica-supported H₃PW₁₂O₄₀ also demonstrated good performance in these reactions.

Keywords: Biomass-based feedstock; cycloaddition; heterogeneous acid catalysis; heteropoly acids; monoterpenes.

* Corresponding author. Tel.: +55 31 34095741; fax: +55 31 34095700.

E-mail address: elena@ufmg.br (E. V. Gusevskaya).

1. Introduction

Mitigating the environmental impact of industrial chemical processes is one of the main topics in modern chemistry, in particular, catalytic chemistry. Although the use of catalytic rather than stoichiometric reactions is already among the requirements of green organic synthesis, the development of environmentally benign catalytic processes remains a challenge. In this connection, the use of renewable reagents and non-toxic biodegradable solvents (or no solvent at all) as well as heterogeneous catalysis, which allows facile catalyst separation and reduction of waste, is particularly important for the design of sustainable eco-friendly catalytic processes.

Numerous terpenic compounds found in essential oils (often as main constituents) are widely used in the fragrance, pharmaceutical and cosmetic industries [1–3]. Besides, terpenes can be chemically transformed into value-added products and therefore represent an abundant feedstock of renewable biomass-based substrates for chemical industry [1–8]. A variety of chemical reactions has been used for the catalytic upgrading of terpenes, such as hydroformylation, oxidation, epoxidation and hydrogenation [4–8]. Acid-catalyzed transformations can also lead to various useful commercial chemicals starting from terpenes [6,9,10]. Most of these processes still use large amounts of mineral acids as catalysts and operate under homogeneous conditions with serious corrosion and waste problems.

Heteropoly acids (HPAs) due to their unique properties represent an attractive and environmentally friendly alternative to conventional acid catalysts such as mineral acids, ion-exchange resins, zeolites and clays [11–13]. First few examples of the application of heteropoly compounds (HPCs) for the transformations of terpenes were published in the 1990s [14–16]. Over the last decade, the interest to this promising topic has greatly increased [13]. HPAs usually show better catalytic activity and selectivity than the conventional acid catalysts and allow for higher turnover numbers to be obtained due to their stronger acidity. The important advantage of using HPAs in catalysis is the possibility to create heterogeneously-catalyzed processes in both non-polar and polar media. In non-polar solvents HPAs are insoluble and can be used directly as bulk and supported catalysts, e.g., HPA/SiO₂. In polar solvents, such as water, lower alcohols, acetone, etc., HPAs themselves are highly soluble, however their acidic salts with large

monovalent cations such as $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) are insoluble and can be applied as heterogeneous acid catalysts. CsPW, possessing strong Brønsted acidity, large surface area and high thermal stability, has been successfully used as a solid acid catalyst in several liquid-phase organic reactions [17–22].

Previously, we have applied HPCs as catalysts in various liquid-phase catalytic reactions of terpenes such as isomerization [21,23–26], etherification/esterification [27–29] and coupling with aldehydes [30,31]. In most of these reactions, HPCs have been used as heterogeneous catalysts in appropriate solvents; some of these reactions have been run under solvent free conditions [26], which is the most desirable within the green chemistry concept. As terpenes are highly reactive under acidic conditions, the use of solvents is usually required to avoid product and/or substrate oligomerization. Moreover, the reactions can be strongly dependent on the solvent nature, for example, α -pinene oxide isomerization [24] and coupling of terpenes with aldehydes [30,31].

The use of HPCs as catalysts for cycloaddition of aldehydes to terpenes has first been disclosed in our recent reports [30,31]. This chemistry represents a promising approach to the synthesis of oxygen-containing heterocyclic compounds [10,32–36], in particular, fragrance bicyclic ethers with oxabicyclo[3.3.1]nonene units [33,34,37]. The latter have attracted much attention as ligands for estrogen receptors involved in many physiological processes, e.g., cell growth regulation. Among the solvents used in the reactions of terpenes with aldehydes, satisfactory results have so far been obtained only in toxic and rigorously regulated solvents such as dichloromethane and 1,2-dichloroethane [30–35]. For this reason, our recent studies have been aimed at the search for environmentally friendly reaction media to substitute the chlorinated solvents. Another aim is to extend the scope of substrates to biorenewable aldehydes, i.e., to create processes in which both reagents are derived from biomass.

Recently, organic carbonates, in particular DEC and dimethylcarbonate (DMC), have attracted significant interest as green reagents and solvents in organic synthesis due to their biodegradability and low toxicity [43–45]. The production of DEC and DMC does not involve harmful reagents and their degradation does not produce toxic waste or emission of volatile organic compounds as their building block is carbon dioxide. DEC and DMC are both aprotic,

weakly basic and low polar solvents (dielectric constant, $\epsilon = 2.8$ for DEC and 3.1 for DMC). Also they have relatively low boiling points compared to other organic carbonates, which allows for their easy distillation from reaction media (b.p. = 126 °C for DEC and 90 °C for DMC).

Here, we describe the cycloaddition reactions of monoterpenes with a series of aldehydes in the presence of silica-supported tungstophosphoric acid $H_3PW_{12}O_{40}$ (HPW) and bulk CsPW as heterogeneous catalysts. Along with conventional 1,2-dichloroethane, these reactions were performed in non-toxic biodegradable “green” organic solvents such as diethylcarbonate (DEC) and dimethylcarbonate (DMC), as well as biomass-derived 2-methyltetrahydrofuran (MeTHF). The following monoterpenes and monoterpene alcohols were used as the substrates: limonene (**1**), α -terpineol (**2**), α -pinene (**3**), β -pinene (**4**), linalool (**5**) and nerol (**6**). As the aldehydes, biomass-derived cuminaldehyde (**7**) and *trans*-cinnamaldehyde (**8**), available from essential oils of eucalyptus and cinnamon, respectively, were used along with crotonaldehyde (**9**) and benzaldehyde (**10**).

2. Experimental

2.1. Chemicals

All chemicals used for the preparation of catalysts and catalytic tests as well as reaction substrates were acquired from Aldrich, except Aerosil 300 silica, which was from Degussa.

2.2. Characterization techniques

The catalysts were characterized by ^{31}P MAS NMR (Bruker Avance DSX 400 NMR, room temperature, spinning rate of 4 kHz, 85% H_3PO_4 as the reference), X-ray diffraction (XRD, Rigaku Geigerflex-3034 diffractometer with $CuK\alpha$ radiation) and nitrogen physisorption (Micromeritics ASAP 2010 instrument). The content of tungsten and phosphorus in the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP) on a Spectro Ciros CCD instrument.

2.3. Catalyst preparation and characterization

Silica-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW/ SiO_2) was prepared by wet impregnation of Aerosil 300 (BET surface area of $300 \text{ m}^2\text{g}^{-1}$) with an aqueous HPW solution and dried at $130^\circ\text{C}/0.2\text{--}0.3$ Torr for 1.5 h, as described previously [38]. The BET surface area of the prepared catalyst was $200 \text{ m}^2\text{g}^{-1}$, the pore volume $0.53 \text{ cm}^3\text{g}^{-1}$ and the average pore diameter 144 \AA . The ^{31}P MAS NMR spectrum of HPW/ SiO_2 showed only one peak at ca. -15 ppm, characteristic of HPW [39]. As shown by XRD, only a small amount of HPW crystalline phase was present on the catalyst surface, with most of HPW being finely dispersed. The HPW content in the catalyst was 20 wt%.

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) was synthesized by dropwise addition of aqueous solution of cesium carbonate (0.47 M) to aqueous solution of HPW (0.75 M) at room temperature with stirring, as described previously [40]. The precipitated CsPW was aged in the aqueous mixture for 48 h at room temperature and dried in a rotary evaporator at $45^\circ\text{C}/3$ kPa than in an oven at $150^\circ\text{C}/0.1$ kPa for 1.5 h. The BET surface area of the prepared catalyst was $111 \text{ m}^2\text{g}^{-1}$, the pore volume $0.07 \text{ cm}^3\text{g}^{-1}$, and the average pore diameter 24 \AA . The acid properties of the prepared catalysts, CsPW and HPW/ SiO_2 , have been studied calorimetrically by ammonia and pyridine adsorption and discussed previously [41,42].

2.4. Catalytic reactions

The catalytic tests were run under air in a 10 mL glass reactor equipped with a reflux condenser to avoid solvent evaporation. In a typical run, a mixture of the substrate (0.45–1 mmol), aldehyde (0.45–1.50 mmol), dodecane (GC internal standard, 0.30 mmol) and the catalyst HPW/ SiO_2 (10–20 mg, 0.70–1.40 μmol of HPW) or CsPW (10–30 mg, 3.0–9.0 μmol), in a specified solvent (3.0 mL) was magnetically stirred at $25\text{--}80^\circ\text{C}$ for a specified time. The reaction mixture was periodically analyzed by gas chromatography (GC, Shimadzu 17 instrument, Carbowax 20 M capillary column, flame ionization detector). Conversions and selectivities were calculated based on the monoterpene substrate (limiting reagent) using dodecane as the internal standard. The difference in mass balance (if any) was attributed to high-boiling products (probably oligomers which could not be detected by GC). In order to control any contribution of homogeneous reactions and catalyst leaching, the catalyst was separated from the reaction mixture by centrifugation (20°C , 18 000 rpm) and the reaction was allowed to proceed with another portion of monoterpene substrate. The lack of additional substrate conversion indicated

the absence of any significant catalyst leaching. In addition, the tungsten content in supernatants was analyzed by atomic absorption spectroscopy (Hitachi-Z8200 spectrometer). For catalyst reuse, the catalyst was separated and washed several times with chloroform.

Reaction products were isolated by a column chromatography (silica gel 60) using mixtures of hexane and CH₂Cl₂ as eluents and identified by GC-MS (Shimadzu QP2010-PLUS spectrometer, 70 eV), ¹H, and ¹³C-NMR (Bruker 400 MHz spectrometer, CDCl₃, TMS).

Compound 11 (new compound): MS (70 eV, EI): *m/z* 284 (0.2) [M⁺], 266 (0.2) [M⁺-H₂O], 149 (19), 136 (40%), 121 (10%), 93 (100%), 92 (48%), 91 (18%), 79 (10%), 77 (11%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS), δ=0.88 (s, 3H; C⁷H₃), 1.21 (s, 6H; C¹⁹H₃ and C²⁰H₃), 1.32 (s, 3H; C¹⁰H₃), 1.37 (s, 3H; C⁹H₃), 1.55 (br.s., 1H; C⁴H), 1.65–1.75 (m, 1H; C⁵HH), 2.00–2.15 (m, 1H; C³HH), 2.18 (br.s, 1H; C⁶H), 2.30–2.45 (m, 2H; C³HH and C⁵HH), 2.86 (br.s., 1H; C¹⁸H), 4.85 (br.s., 1H; C¹¹H), 5.44 (br.s., 1H; C²H), 7.12 (br.s., 2H; C¹⁴H and C¹⁶H), 7.22 ppm (br.s., 2H; C¹³H and C¹⁷H). ¹³C NMR (100 MHz, CDCl₃, 25°C, TMS), δ=23.97 (C⁷), 24.07 (C⁹), 28.70 (C¹⁰), 24.18 (C¹⁹ and C²⁰), 27.73 (C³), 28.35 (C⁵), 33.79 (C¹⁸), 33.99 (C⁴), 41.49 (C⁶), 74.13 (C¹¹), 75.22 (C⁸), 123.14 (C²), 125.57 and 125.81 (C¹³, C¹⁴, C¹⁶ and C¹⁷), 133.39 (C¹), 140.24 (C¹²), 147.23 ppm (C¹⁵). For atom numbering see Scheme 1.

Compound 12 (new compound), major isomer (shorter GC retention time): MS (70 eV, EI): *m/z* 268 (0.1) [M⁺], 136 (25%), 133 (35), 121 (10%), 115 (10), 94 (10), 93 (100%), 92 (41%), 91 (20%), 77 (12%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS), δ=1.28 (s, 3H; C¹⁰H₃), 1.36 (s, 3H; C⁹H₃), 1.45-1.55 (m, 1H; C⁴H), 1.65–1.75 (m, 2H; C³HH and C⁵HH), 1.68 (s, 3H; C⁷H₃), 2.05 (br.s, 1H; C⁶H), 2.15–2.25 (m, 1H; C⁵HH), 2.30–2.40 (m, 1H; C³HH), 4.45 (br.d, ³J=6.4 Hz, 1H; C¹¹H), 5.54 (br.s., 1H; C²H), 6.15 (dd, ³J=6.4 Hz, ³J=16.1 Hz, 1H; C¹²H), 6.55 (d, ³J=16.1 Hz, 1H; C¹³H), 7.17 (t, ³J=7.3 Hz, 1H; C¹⁷H), 7.26 (t, ³J=7.3 Hz, 2H; C¹⁶H and C¹⁸H), 7.35 ppm (br.s, 2H; C¹⁵H and C¹⁹H). ¹³C NMR (100 MHz, CDCl₃, 25°C, TMS), δ=24.13 (C⁹), 25.08 (C⁷), 28.65 (C¹⁰), 27.78 (C³), 28.06 (C⁵), 34.05 (C⁴), 40.53 (C⁶), 74.50 (C¹¹), 75.44 (C⁸), 123.84 (C²), 126.38 (C¹⁵ and C¹⁹), 127.19 (C¹⁷), 128.46 (C¹⁶ and C¹⁸), 128.95 (C¹³), 131.27 (C¹²), 133.26 (C¹), 137.29 ppm (C¹⁴). Minor isomer (longer GC retention time): MS (70 eV, EI): *m/z* 268 (0.1) [M⁺], 136 (35%), 133 (41%), 121 (11%), 115 (9%), 94 (13%), 93 (100%), 92 (12%), 91 (21%), 80 (11%), 79 (11%), 77 (14%). For atom numbering see Scheme 1.

Compound 13: MS (70 eV, EI): m/z 206 (0.5) [M^+], 136 (50%), 121 (18%), 93 (100%), 92 (40%), 91 (20%), 77 (15%). For NMR data see [30].

Compound 14: MS (70 eV, EI): m/z 242 (0.5) [M^+], 136 (60%), 121 (12%), 93 (100%), 92 (50%), 91 (20%), 77 (11%). For NMR data see [31].

3. Results and discussion

3.1. Reactions of terpenes with cuminaldehyde

Cuminaldehyde (**7**) is a naturally occurring monoterpene compound found in various essential oils such as of eucalyptus and myrrh oils. Due to the persistent pleasant smell cuminaldehyde is commercially used in perfumes and other cosmetics [1]. The addition of cuminaldehyde to other monoterpenes could result in oxygenated diterpenic compounds with interesting fragrance properties and/or biological activity.

Representative data on the reaction between cuminaldehyde (**7**) and limonene (**1**) in the presence of HPW/SiO₂ and CsPW catalysts in various solvents are collected in Table 1. In blank experiments with no catalyst added, limonene was virtually stable under the conditions used. The major reaction product was compound **11**; it was identified by MS and NMR as diterpenic ether shown in Schemes 1 and 2. The structure of **11** suggests that it results from the cyclization coupling of cuminaldehyde and limonene in which course the carbonyl carbon atom of the aldehyde bounds to the endocyclic allylic position of limonene and the oxygen atom to the central atom of the limonene isopropyl fragment. The selectivity for **11** was strongly affected by the reaction time and other reaction variables. Along with **11**, isomeric *para*-menthenic terpenes were formed from limonene under acidic conditions (mainly α -terpinene, γ -terpinene and terpinolene). Isolated ether **11** is a new compound, as far as we know, with a pleasant woody smell.

In 1,2-dichloroethane solutions in the presence of HPW/SiO₂ (0.1 wt% per the whole reaction mixture), 37% of limonene was converted in 1 h at 40 °C; however, the selectivity for **11** was only 29%, with other isomers of limonene being responsible for the rest of mass balance

(Table 1, run 1). Further optimization of substrate concentration, catalyst loading and reaction temperature allowed us to achieve 80% selectivity for the desired ether **11** at nearly complete limonene conversion (Table 1, run 5). High turnover numbers obtained (up to 1000 per mole of HPW) illustrate high catalyst stability under the reaction conditions. Cuminaldehyde was used in a 3-fold excess in order to capture the limonene molecule thus disfavoring other acid-catalyzed transformations such as isomerization and oligomerization. Non-reacted aldehyde can be recovered and used in subsequent reaction cycles.

Important goal of the present work is to find viable eco-friendly alternatives for chlorinated solvents, which have been the solvents of choice for the reactions between aldehydes and terpenes in all previous reports [30–35]. After our previous failed attempts to replace 1,2-dichloroethane in the reaction of benzaldehyde with terpenes by various conventional less hazardous solvents [31], we were very pleased to discover that limonene readily reacted with cuminaldehyde in diethylcarbonate (DEC) in the presence of HPW/SiO₂ catalyst, giving the same major product as in 1,2-dichloroethane. The reaction occurred with almost the same selectivity, albeit slower, probably due to stronger association of ionic pairs in less polar DEC (Table 1, cf. runs 6 and 5). The CsPW catalyst, also performed very well in the reaction of cuminaldehyde with limonene showing 85% selectivity for **11** at complete limonene conversions in DEC (Table 1, run 7–9) and 80% in DMC (Table 1, run 10).

Recently, organic carbonates, in particular DEC and dimethylcarbonate (DMC), have attracted significant interest as green reagents and solvents in organic synthesis due to their biodegradability and low toxicity [43–45]. The production of DEC and DMC does not involve harmful reagents and their degradation does not produce toxic waste or emission of volatile organic compounds as their building block is carbon dioxide. DEC and DMC are both aprotic, weakly basic and low polar solvents (dielectric constant, $\epsilon = 2.8$ for DEC and 3.1 for DMC). Also they have relatively low boiling points compared to other organic carbonates, which allows for their easy distillation from reaction media (b.p. = 126 °C for DEC and 90 °C for DMC).

Although HPW and CsPW are insoluble in low polar DEC and DMC (as well as in 1,2-dichloroethane), the stability of both towards leaching under reaction conditions was carefully verified by special experiments. After runs 6 and 7 (Table 1), the reaction mixtures were centrifuged for 20 min (20 °C, 18 000 rpm) in order to separate the catalyst. Tungsten content in

the supernatants was determined by atomic absorption spectroscopy. In addition, to control HPW and CsPW leaching the activities of the supernatants were checked by allowing the reactions to proceed after adding new limonene portions. The supernatant after the run with CsPW (Table 1, run 7) showed no additional conversion and the tungsten content corresponded to less than 1.5% loss of CsPW. On the other hand, the supernatant after the run with HPW/SiO₂ (Table 1, run 6) contained 18% of tungsten originally used for the reaction; moreover, the supernatant was catalytically active converting 20% of the freshly added limonene in 5 h. Given the low solubility of HPW in non-polar solvents, we suspected that the problem was the separation of HPW/SiO₂ from the reaction mixture rather than HPW leaching. Indeed, a longer centrifugation (1.5 h) allowed for better removal of HPW/SiO₂ and the supernatant was no longer active in the limonene conversion. Although both HPW/SiO₂ and CsPW catalysts performed truly heterogeneously, taking into account the easier CsPW separation, further work in DEC/DMC solutions was carried out with the CsPW catalyst.

The reaction of cuminaldehyde with α -terpineol (**2**), another *para*-menthenic terpene, in the presence of HPW/SiO₂ or CsPW catalysts mainly gave the same ether **11** (Table 2). High selectivity of 90% at a nearly complete α -terpineol conversion was observed in 1,2-dichloroethane solutions at 40 °C, whereas at 50 and 60 °C the selectivity was slightly lower (ca. 80%) (Table 2, run 1 vs. runs 2 and 3). Limonene and other *para*-menthenes (α -terpinene, γ -terpinene and terpinolene) were detected as minor by-products. Unfortunately, the amount of *para*-menthenes did not significantly decrease at longer reaction times, when the reaction mixture was left in contact with the catalyst after complete conversion of α -terpineol (Table 1, runs 2 and 3). The reaction also readily occurred in the presence of CsPW catalyst (Table 2, run 4).

DEC and DMC also proved to be excellent alternatives for 1,2-dichloroethane to perform the reaction of cuminaldehyde with α -terpineol (Table 2, runs 5–10). After optimization of reaction variables, complete conversions of α -terpineol were obtained for reasonably short reaction times with 85–87% selectivity for the desired product **11** and high TONs (Table 2, runs 9 and 10). Noteworthy, the reactivity of α -terpineol was much higher than that of limonene; under similar reaction conditions, 98% of α -terpineol was consumed within 1 h, compared to only 48% of limonene (run 5 in Table 2 vs. in run 8 in Table 1). On the other hand, the reaction

with limonene was more selective to the desired ether **11** than the reaction with α -terpineol. The CsPW catalyst could be easily separated by centrifugation and reused. In run **XX**, the catalyst was reused two times after washing with chloroform without any significant decrease in activity and selectivity.

The reaction can also be carried out in 2-methyltetrahydrofuran (MeTHF), which is considered an eco-friendly biomass-based alternative to chlorinated solvents [46,47]. MeTHF is produced from furfural or levulinic acid, which are renewable precursors available from lignocellulosic biomass. Among other properties of MeTHF, which bring it to the list of modern green solvents, are its abiotical degradability, low toxicity and better stability compared to other ether solvents. MeTHF and 1,2-dichloroethane have similar polarity ($\epsilon = 10.4$ and 7.0 , respectively); however, MeTHF possesses higher Lewis basicity, which could decrease the acid strength of acid catalysts. As expected, the reaction of cuminaldehyde with α -terpineol occurred slower in MeTHF than in DEC and DMC, nevertheless it had excellent 96% selectivity for product **11** (Table 2, run 11 vs runs 9 and 10). At a higher temperature of $70\text{ }^\circ\text{C}$, the reaction in MeTHF could be run faster to be completed within 5 h with 90% selectivity for ether **11** and high TONs (Table 2, run 12). Encouraged by this result, we tested the reaction with less reactive limonene in MeTHF solutions and also observed efficient catalytic performance of CsPW (Table 1, run 11). These two reactions represent examples of truly green synthetic processes which occur with 100% atom efficiency under mild conditions and use only biomass-derived renewable organic materials – both the reagents and the solvent.

α -Pinene (**3**), one of the more widespread terpenic compounds available from turpentine oils obtained from coniferous trees, also gives ether **11** with good selectivity reacting with cuminaldehyde in the presence of HPW/SiO₂ or CsPW (Table 3). The reaction readily occurred in 1,2-dichloroethane with high TONs and 80% selectivity for **11** at a complete substrate conversion (Table 3, run 1). 1,2-Dichloroethane can be replaced by DEC (Table 3, runs 2 and 3). The CsPW catalyst is preferred due to its easier separation from DEC solutions as compared to HPW/SiO₂ (Table 2, runs 4–7). It is important that in most cases the selectivity increased with reaction time due to transformation of isomeric monoterpenes rapidly formed at early reaction stages to ether **11**.

The same product **11** was obtained in the reaction between cuminaldehyde and β -pinene (**4**) in 1,2-dichloroethane (up to 66% yield) and in DMC (45% yield) (Table 4). β -Pinene reacted under acidic conditions very rapidly even at room temperature (Table 4, run 3), giving **11** and isomeric monoterpenes together with non-detectable (GC) high-boiling by-products. Differently from the examples described above, the selectivity for ether **11** in the reaction with β -pinene did not increase with the reaction time. Two monoterpenic allylic alcohols, linalool (**5**) and nerol (**6**), were also coupled with cuminaldehyde in the presence of CsPW catalyst in DEC solutions to give **11** as the major product. After optimization, ether **11** was obtained from nerol in 62% yield, whereas from linalool only in 34% yield due to formation of significant amounts of isomeric *para*-menthenes and high-boiling oligomers (Table 5, runs 1 and 2, respectively).

3.2. Reactions of terpenes with other aldehydes in diethylcarbonate solutions

Representative results for the reactions of limonene and α -terpineol with *trans*-cinnamaldehyde (**8**), crotonaldehyde (**9**) and benzaldehyde (**10**) in DEC solutions are collected in Table 5 (runs 3–8). After optimization, these reactions gave the corresponding oxabicyclo[3.3.1]nonene compounds in good to excellent yields (all had pleasant fragrance characteristics after isolation).

Cinnamaldehyde is a natural product occurring in high concentrations in cinnamon essential oils, predominately as *trans* (E) isomer. Due to its pleasant smell and low toxicity this compound has found numerous commercial applications as a flavoring agent in food and perfume industries and is also used as a fungicide and insecticide agent in agriculture. Cycloaddition of *trans*-cinnamaldehyde to limonene and α -terpineol resulted in the same product, oxabicyclic compound **12** (Table 5, runs 3 and 4; for the structure of **12** see Scheme 1). As far as we know, this is a new compound; two stereoisomers of **12** with virtually the same mass spectra were detected in the reaction solutions, in most cases in the ratio of ca. 9/1.

Cycloaddition of crotonaldehyde (**9**) and benzaldehyde (**10**) to either limonene or α -terpineol in DEC gave analogous products **13** and **14** (Scheme 1), respectively, with 80–90 % selectivity at nearly complete substrate conversions (Table 5, runs 5–8). These results represent additional evidence for the viability of organic carbonates as green solvents in the reactions of

terpenic compounds with aldehydes to replace toxic chlorinated solvents – the only class of solvents which has shown satisfactory performance in all previous studies.

3.3. Proposed mechanism

A plausible mechanism for the cycloaddition of aldehydes to monoterpenic compounds is shown in Scheme 3. Given that all monoterpenes form the same type of product (**11** – **14**) regardless of the aldehyde used, it is conceivable that α -terpenyl carbenium ion **A** is a common intermediate in all these cycloadditions. Protonation of limonene and protonation/dehydration of α -terpineol give the carbocation **A** directly. Other substrates, such as α -pinene, β -pinene, linalool and nerol, first give different carbenium ions under acidic conditions (their structures are not shown in Scheme 3); these can isomerize rapidly into carbocation **A**, which seems to be more stable under the reaction conditions. Interaction of the aldehyde with carbenium ion **A** results in formation of oxocarbenium intermediate **B**. Subsequent oxonium-ene cyclization via intramolecular attack of the carbon-carbon double bond on the oxocarbenium ion results in oxabicyclic products **11-14**.

In principle, carbenium ion **A** can lose a proton before interacting with aldehyde to give other *para*-menthenic terpenes such as terpinolene, α -terpinene and γ -terpinene, detected as main by-products in our systems. Interaction of the ionic intermediates with the monoterpene substrates can also lead to high molecular weight by-products (herein referred to as oligomers). To minimize these undesirable transformations and improve the selectivity for ethers **11-14**, a large (3-fold) excess of aldehydes was used in our reaction protocols, which allowed efficient trapping of intermediate **A**.

4. Conclusions

The acidic Cs salt of tungstophosphoric heteropoly acid, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, is excellent solid acid catalyst for liquid-phase cycloaddition reactions between naturally occurring monoterpenes and aldehydes, including also biomass-derived aldehydes. The reactions result in theoxabicyclo[3.3.1]nonene compounds, which are difficult to obtain by conventional synthetic methods. These compounds are potentially useful for the fragrance and pharmaceutical industries. The catalyst does not suffer from leaching and can be easily separated from the reaction media.

Relatively low boiling points of the solvents used allow for their easy removal by distillation. High atom economy, mild reaction conditions, low catalyst loadings and the use of non-toxic biodegradable “green” organic solvents, such as dimethylcarbonate, diethylcarbonate and biomass-derived 2-methyltetrahydrofuran, are important advantages of the developed environmentally benign catalytic protocol for upgrading bio-renewable materials into value-added products.

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Scheme and Table captions

Scheme 1. Products of cycloaddition of cuminaldehyde (**11**), *trans*-cinnamaldehyde (**12**), crotonaldehyde (**13**) and benzaldehyde (**14**) to monoterpenes.

Scheme 2. Cycloaddition of limonene (**1**), α -terpineol (**2**), α -pinene (**3**), β -pinene (**4**), linalool (**5**) and nerol (**6**) to cuminaldehyde (**7**) in the presence of HPW/SiO₂ or CsPW.

Scheme 3. Proposed mechanism of cycloaddition of limonene (**1**), α -terpineol (**2**), α -pinene (**3**), β -pinene (**4**), linalool (**5**) and nerol (**6**) to cuminaldehyde (**7**), *trans*-cinnamaldehyde (**8**), crotonaldehyde (**9**) and benzaldehyde (**10**).

Table 1. Cycloaddition of cuminaldehyde (**7**) to limonene (**1**).^a

Table 2. Cycloaddition of cuminaldehyde (**7**) to α -terpineol (**2**).^a

Table 3. Cycloaddition of cuminaldehyde (**7**) to α -pinene (**3**).^a

Table 4. Cycloaddition of cuminaldehyde (**7**) to β -pinene (**4**).^a

Table 5. CsPW catalyzed cycloaddition of aldehydes to monoterpenes in diethylcarbonate solutions.^a

Table 1.Cycloaddition of cuminaldehyde (**7**) to limonene (**1**).^a

Run	Catalyst (mg)	HPW or CsPW (μmol)	<i>T</i> ($^{\circ}\text{C}$)	Time (h)	Conversion (%)	Selectivity for 11 (%)	TON ^b
Solvent: 1,2-dichloroethane							
1	HPW/SiO ₂ (10)	0.70	40	1	37	29	
				8	70	60	1000
2	HPW/SiO ₂ (15)	1.05	40	1	43	84	
				8	80	82	760
3	HPW/SiO ₂ (15)	1.05	50	1	62	78	
				5	98	82	935
4	HPW/SiO ₂ (20)	1.40	50	1	75	80	
				5	97	82	695
5 ^c	HPW/SiO ₂ (20)	1.40	50	1	63	80	
				5	95	80	1020
Solvent: diethylcarbonate (DEC)							
6 ^c	HPW/SiO ₂ (20)	1.40	60	1	57	80	
				8	91	82	975
7	CsPW (30)	9.00	60	1	30	84	
				9	70	85	80
8 ^d	CsPW (30)	9.00	60	1	48	82	
				3	100	85	110
9	CsPW (30)	9.00	70	1	97	80	
				2	100	80	100
Solvent: dimethylcarbonate (DMC)							
10	CsPW (30)	9.00	70	1	97	73	
				2	100	80	110
Solvent: 2-methyltetrahydrofuran (MeTHF)							
11	CsPW (30)	9.00	70	2	70	55	
				7	99	81	110

^aLimonene, 1.00 mmol; cumenaldehyde, 3.00 mmol; total volume, 3.0 mL. Conversion and selectivity (based on limonene) were obtained by GC. *Para*-menthenic monoterpenes (terpinolene, α -terpinene and γ -terpinene) accounted for the rest of the mass balance.^b TON (turnover number) was calculated as the moles of limonene reacted per mole of HPW or CsPW. ^c Limonene, 1.50 mmol. ^d Limonene, 0.45 mmol; cumenaldehyde, 2.25 mmol.

Table 2.Cycloaddition of cuminaldehyde (**7**) to α -terpineol (**2**).^a

Run	Catalyst (mg)	HPW or CsPW (μ mol)	<i>T</i> (°C)	Time (h)	Conversion (%)	Selectivity for 11 (%)	TON ^b
Solvent: 1,2-dichloroethane							
1 ^c	HPW/SiO ₂ (15)	1.05	40	1	71	91	
				2	90	90	386
2 ^c	HPW/SiO ₂ (15)	1.05	50	1	96	82	
				2	100	82	428
3 ^c	HPW/SiO ₂ (15)	1.05	60	0.5	98	77	
				2	100	76	428
4 ^c	CsPW (30)	9.00	60	1	99	72	
				5	100	72	50
Solvent: diethylcarbonate (DEC)							
5 ^c	CsPW (30)	9.00	60	1	98	62	50
6 ^c	CsPW (30)	9.00	50	1	96	70	50
7 ^c	CsPW (30)	9.00	50	3	98	75	110
8	CsPW (10)	3.00	50	1	40	89	
				12	90	93	300
9	CsPW (10)	3.00	60	1	69	88	
				5	98	87	330
Solvent: dimethylcarbonate (DMC)							
10	CsPW (10)	3.00	60	1	66	77	
				5	97	85	330
Solvent: 2-methyltetrahydrofuran (MeTHF)							
11	CsPW (10)	3.00	60	5	20	96	66
12	CsPW (10)	3.00	70	1	20	90	
				5	98	90	330

^a α -Terpineol, 1.00 mmol; cuminaldehyde, 3.00 mmol; total volume, 3.0 mL. Conversion and selectivity (based on α -terpineol) were obtained by GC. *Para*-menthenic monoterpenes (limonene, terpinolene, α -terpinene and γ -terpinene) accounted for the rest of the mass balance.

^b TON (turnover number) was calculated as the moles of α -terpineol reacted per mole of HPW or CsPW.

^c α -Terpineol, 0.45 mmol; cumenaldehyde, 2.25 mmol.

Table 3.Cycloaddition of cuminaldehyde (**7**) to α -pinene (**3**).^a

Run	Catalyst (mg)	HPW or CsPW (μ mol)	<i>T</i> ($^{\circ}$ C)	Time (h)	Conversion (%)	Selectivity for 11 (%)	TON ^b
Solvent: 1,2-dichloroethane							
1	HPW/SiO ₂ (15)	1.05	50	0.25	100	80	
				2	100	80	952
Solvent: diethylcarbonate (DEC)							
2	HPW/SiO ₂ (15)	1.05	50	0.25	91	68	
				2	100	75	952
3	HPW/SiO ₂ (15)	1.05	60	0.25	99	67	
				2	100	72	952
4	CsPW (15)	4.50	60	0.25	99	51	
				2	100	68	220
5	CsPW (15)	4.50	50	2	99	61	300
6	CsPW (10)	3.00	50	2	89	54	222
7	CsPW (30)	9.00	40	5	100	68	111

^a α -Pinene, 1.00 mmol; cuminaldehyde, 3.00 mmol; total volume, 3.0 mL. Conversion and selectivity (based on α -pinene) were obtained by GC. *Para*-menthenic monoterpenes (limonene, terpinolene, α -terpinene and γ -terpinene) accounted for the rest of the mass balance.

^b TON (turnover number) was calculated as the moles of α -pinene reacted per mole of HPW or CsPW.

Table 4.Cycloaddition of cuminaldehyde (**7**) to β -pinene (**4**).^a

Run	Catalyst (mg)	HPW or CsPW (μ mol)	<i>T</i> ($^{\circ}$ C)	Time (h)	Conversion (%)	Selectivity for 11 (%)	TON ^b
Solvent: 1,2-dichloroethane							
1	HPW/SiO ₂ (15)	1.05	50	0.25	100	66	950
2	HPW/SiO ₂ (10)	0.70	50	0.25	100	65	1430
3	HPW/SiO ₂ (10)	0.70	25	0.25	100	56	1430
4	CsPW (30)	9.00	50	0.5	100	54	110
Solvent: dimethylcarbonate (DMC)							
5	CsPW (30)	9.00	50	0.5	100	45	110
6	CsPW (10)	3.00	50	0.5	96	30	320

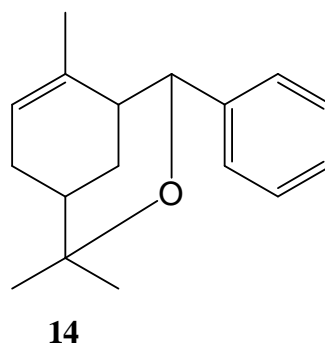
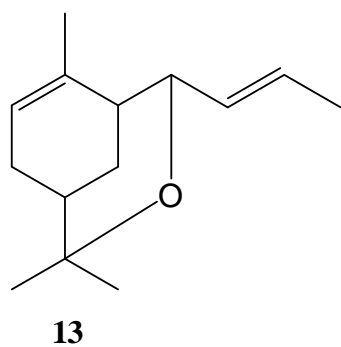
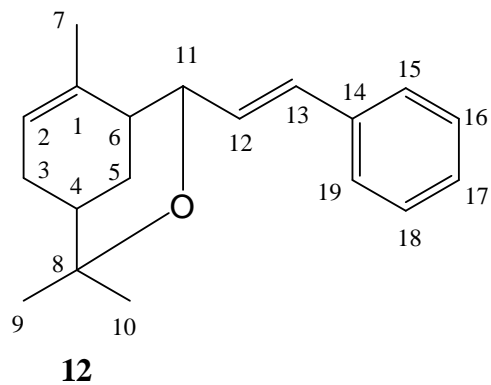
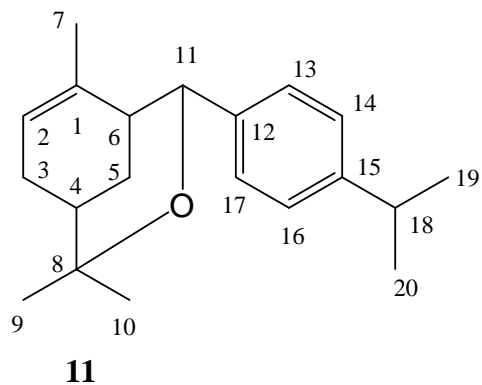
^a β -Pinene, 1.00 mmol; cuminaldehyde, 3.00 mmol; total volume, 3.0 mL. Conversion and selectivity (based on β -pinene) were obtained by GC. *Para*-menthenic monoterpenes (limonene, terpinolene, α -terpinene and γ -terpinene) along with oligomerization products (not detectable by GC) accounted for the rest of the mass balance.

^b TON (turnover number) was calculated as the moles of β -pinene reacted per mole of HPW or CsPW.

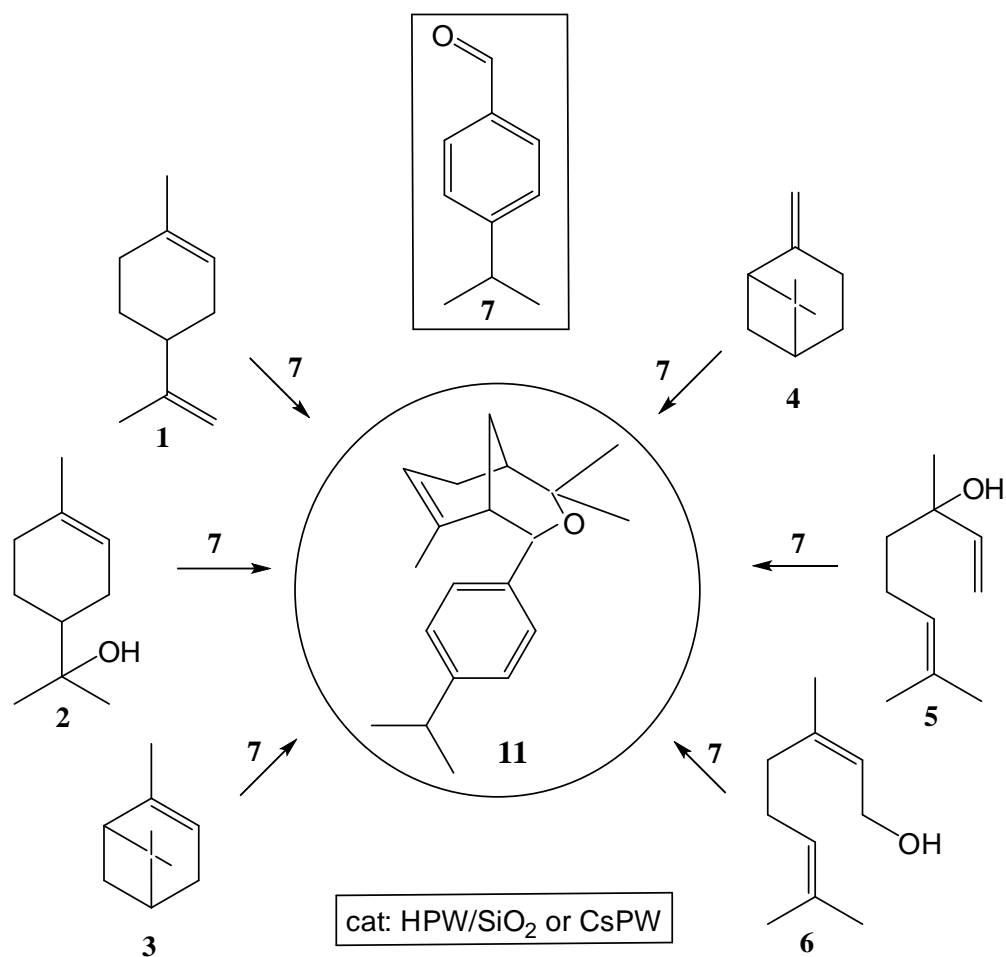
Table 5.CsPW catalyzed cycloaddition of aldehydes to monoterpenes in diethylcarbonate solutions.^a

Run	Substrate	Aldehyde	CsPW (μmol)	<i>T</i> ($^{\circ}\text{C}$)	Time (h)	Conv ersion (%)	Product	Selec tivity (%)	TON ^b
1	Linalool (5)	Cuminaldehyde (7)	9	50	3	100	11	34	110
2	Nerol (6)	Cuminaldehyde (7)	9	60	3	100	11	62	110
3 ^c	Limonene (1)	Cinnamaldehyde (8)	9	50	9	90	12	90	45
4	α -Terpineol (2)	Cinnamaldehyde (8)	3	70	5	95	12	85	320
5	Limonene (1)	Crotonaldehyde (9)	9	80	8	90	13	81	100
6	α -Terpineol (2)	Crotonaldehyde (9)	3	60	7	90	13	80	300
7	Limonene (1)	Benzaldehyde (10)	3	60	12	92	14	86	300
8	α -Terpineol (2)	Benzaldehyde (10)	3	60	6	98	14	91	330

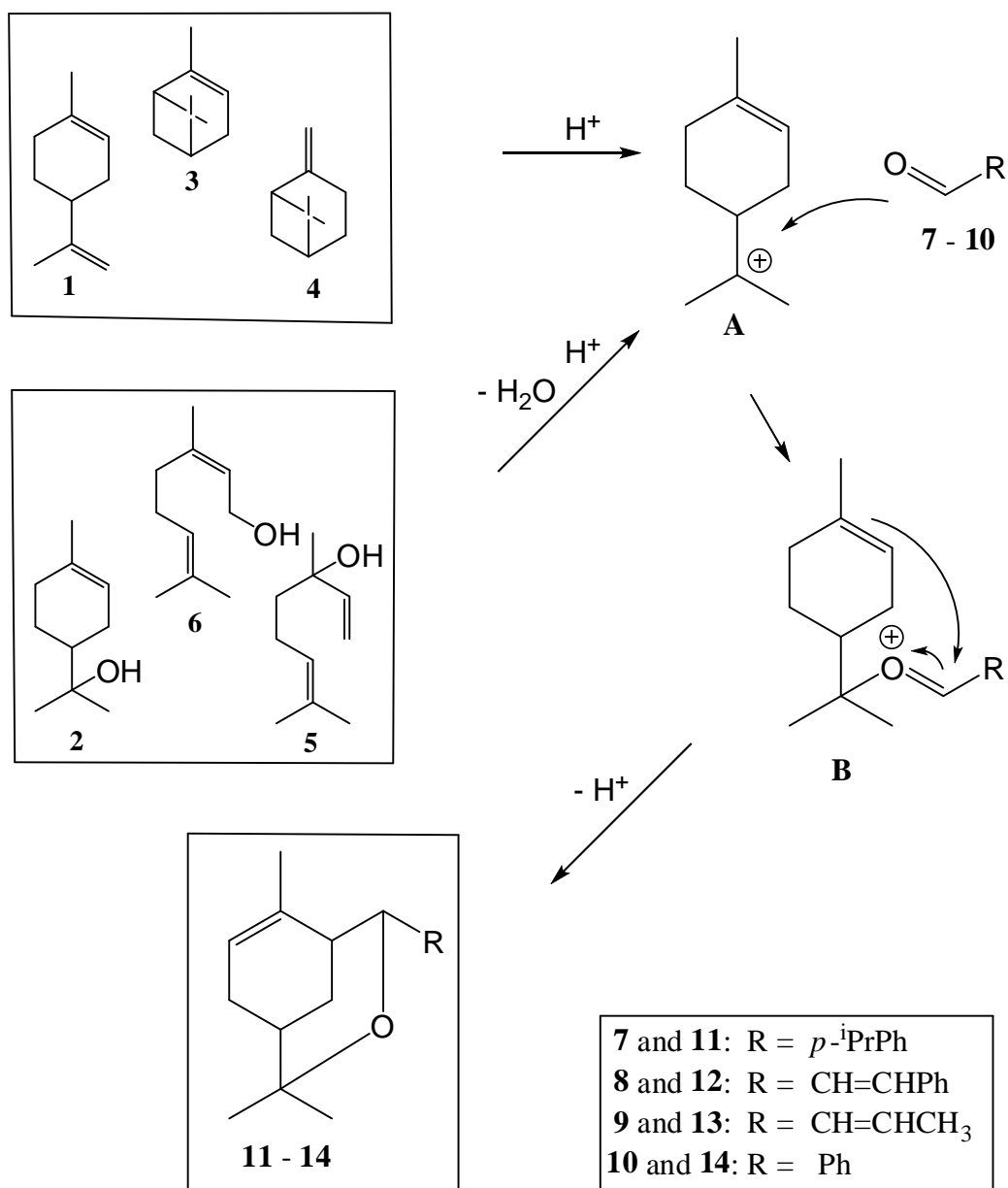
^aSubstrate, 1.00 mmol; aldehyde, 3.00 mmol; CsPW, 10 or 30 mg (3 or 9 μmol); total volume, 3.0 mL. Conversion and selectivity (based on the reacted substrate) were obtained by GC. *Para*-menthenic monoterpenes mainly accounted for the rest of the mass balance. ^bTON (turnover number) was calculated as the moles of the substrate reacted per mole of CsPW. ^c Substrate, 0.45 mmol; aldehyde, 2.25 mmol.



Scheme 1. Products of cycloaddition of cuminaldehyde (**11**), *trans*-cinnamaldehyde (**12**), crotonaldehyde (**13**) and benzaldehyde (**14**) to monoterpenes.



Scheme 2. Cycloaddition of limonene (1), α -terpineol (2), α -pinene (3), β -pinene (4), linalool (5) and nerol (6) to cuminaldehyde (7) in the presence of HPW/SiO₂ or CsPW.



Scheme 3. Proposed mechanism of cycloaddition of limonene (1), α -terpineol (2), α -pinene (3), β -pinene (4), linalool (5) and nerol (6) to cuminaldehyde (7), *trans*-cinnamaldehyde (8), crotonaldehyde (9) and benzaldehyde (10).