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Coupling of monoterpene alkenes and alcohols with benzaldehyde catalyzed by silica-supported tungstophosphoric heteropoly acid

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ABSTRACT

The reactions of biomass-based substrates, i.e., limonene, α -pinene, β -pinene, terpinolene, α -terpineol, nerol and linalool, with benzaldehyde in the presence of tungstophosphoric heteropoly acid $H_3PW_{12}O_{40}$ (HPW) supported on silica give an oxabicyclo[3.3.1]nonene compound with fragrance characteristics in good to excellent yields. The reactions apparently involve the formation of α -terpenyl carbenium ion by the protonation of alkene or dehydration of alcohol followed by the nucleophilic attack of benzaldehyde. The subsequent oxonium-ene cyclization of the resulting oxocarbenium ion gives the oxabicyclic product. The process is an environmentally benign and heterogeneous and can be performed under mild conditions with low catalyst amounts and no significant leaching of active components.

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1. Introduction

Terpenes are natural compounds found in essential oils of various plant materials, frequently, in high concentrations. Although many terpenes themselves are used directly in fragrance, pharmaceutical and cosmetic compositions they can also be chemically transformed into various value-added products [1,2]. In particular, various terpene compounds are industrially produced from more abundant precursors using acid catalysis. Many of these processes are still performed under homogeneous conditions with mineral acids as catalysts and therefore generate large amounts of waste. The search for the heterogeneous catalysts for the acid-catalyzed transformations of terpenes is highly important for the valorization of essential oils as inexpensive bio-renewable feedstock.

Heteropoly acids (HPAs) of the Keggin series, in particular $H_3PW_{12}O_{40}$ (HPW), have received an increasing attention as promising environmentally friendly catalysts in Fine Chemistry [3–6]. HPAs usually show high turnover frequencies as compared to other solid acid catalysts, e.g. ion-exchange resins, zeolites and clays, due to their strong Brønsted acidity. High chemical and thermal stability of HPAs allows achieving impressive turnover

numbers in catalytic processes which often proceed with excellent selectivities. Moreover, HPAs cause less corrosion problems than mineral acids and do not promote undesirable reactions, such as chlorination and sulfonation. HPAs are not soluble in apolar and weakly polar media thus giving the possibility to create efficient heterogeneous processes especially when appropriate solid materials are used for their immobilization.

In our previous works on the catalytic transformation of terpene compounds we successfully used heteropoly compounds as catalysts in various reactions, e.g., isomerization [7–10], hydration and esterification [11–13]. In particular, the addition of aldehydes to terpene compounds, which also can be catalyzed by HPAs, represents a valuable approach to the synthesis of oxygen-heterocyclic compounds [14–19]. As far as we know, the first example of using heteropoly compounds as catalysts in such transformations (cycloaddition of crotonaldehyde to limonene, α -pinene and β -pinene) has been reported in our recent work [20].

In the present work, we have studied the reactions of a series of monoterpenes and monoterpene alcohols with benzaldehyde using silica-supported HPW as the catalyst. The project was aligned with our general program directed to the valorization of natural ingredients of essential oils by catalytic transformations. The following terpene compounds were used as substrates: limonene (1), α -pinene (2), β -pinene (3), terpinolene (4), α -terpinene (5), α -terpineol (6), nerol (7) and linalool (8). The reactions gave the same

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fragrant oxabicyclo[3.3.1]nonene compound potentially useful for various practical applications. Besides interesting fragrant properties, bicyclic ethers containing oxabicyclo[3.3.1]nonene units have been recently described as ligands for estrogen receptors which are involved in many physiological processes, e.g. in the regulation of cell growth [16,19,21].

2. Experimental

2.1. Chemicals

H₃PW₁₂O₄₀ hydrate, benzaldehyde, *R*-(+)-limonene, (–)- α -pinene, (–)- β -pinene, terpinolene, α -terpinene, α -terpineol, nerol and racemic linalool were acquired from Aldrich and Aerosil 300 silica (S_{BET} , 300 m² g⁻¹) from Degussa.

2.2. Characterization techniques

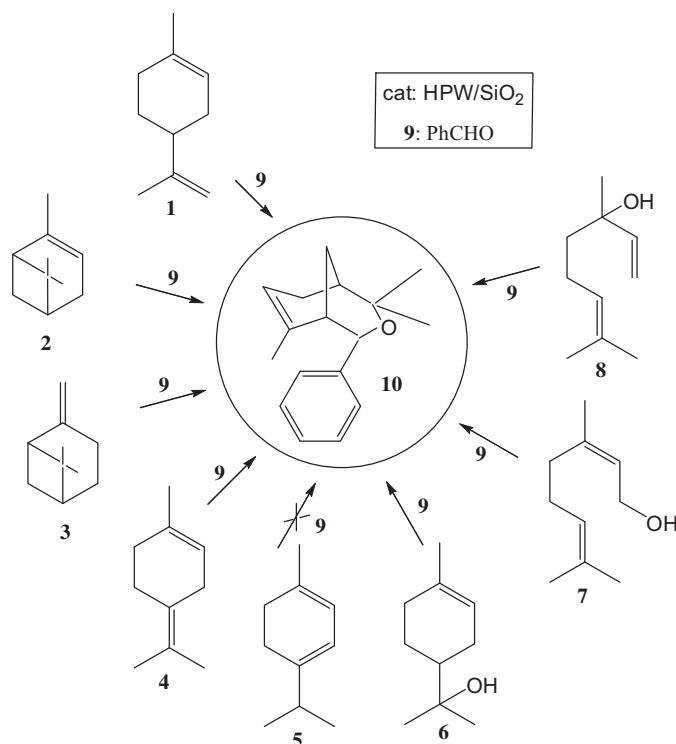
³¹P MAS NMR spectra were collected on a Bruker Avance DSX 400 NMR instrument at ambient temperature and spinning rate of 4 kHz using H₃PO₄ (85%) as the reference. A Rigaku Geigerflex-3034 diffractometer with CuK α radiation was used for the powder X-ray diffraction (XRD). The morphological properties were studied by nitrogen physisorption using a Micromeritics ASAP 2010 instrument at 77 K. The amounts of tungsten and phosphorus in the catalyst were measured by inductively coupled plasma atomic emission spectroscopy (ICP) using a Spectro Ciros CCD instrument.

2.3. Catalyst preparation and characterization

The H₃PW₁₂O₄₀/SiO₂ catalyst (HPW/SiO₂), was synthesized by the impregnation of Aerosil 300 with an aqueous solution of HPW. The content of HPW was 20 wt% (obtained with ICP). The material was calcinated at 130 °C/0.2–0.3 Torr for 1.5 h, as reported previously [22]. The specific surface area determined by the BET method was 200 m² g⁻¹. The average pore diameter and the single point total pore volume were 144 Å and 0.53 cm³ g⁻¹, respectively. The integrity of the Keggin structure was confirmed by ³¹P MAS NMR spectroscopy as the catalyst spectrum consisted of only one peak at ca. –15 ppm, typical for HPW [23]. The XRD analysis revealed only small amounts of the crystalline phase of HPW, with most of HPW being finely dispersed on the catalyst surface.

2.4. Catalytic reactions

The runs were performed in a 10 mL glass vessel using magnetic stirring. When necessary, the reactor was coupled with a condenser to avoid solvent evaporation. In a typical run, a mixture (3.0 mL) of the substrate (0.45–1 mmol), benzaldehyde (0.75–5.00 mmol), undecane as a GC internal standard (0.3 mmol,) and the catalyst (HPW/SiO₂ (2–20 mg 10–75 mg, 0.14–1.40 μ mol of HPW), in 1,2-dichloroethane (or other solvent) was intensely stirred under air at 30–60 °C for the time indicated in the Tables. The reactions were monitored by gas chromatography (GC, Shimadzu 17 instrument, Carbowax 20 M capillary column, flame ionization detector). Periodically, stirring was stopped and a sample of the supernatant was taken after rapid catalyst sedimentation. The conversions and selectivities were calculated based on the converted amounts of the monoterpene substrate using undecane as the internal standard. It was assumed that the formation of high-boiling products (probably oligomers which could not be observed by GC) was responsible for the difference in the mass balance. In order to check the HPW leaching from the silica surface, the catalyst was centrifuged from the reaction mixture and the reaction was continued. The additional amounts of the substrate were added to the supernatant



Scheme 1. Reactions of limonene (1), α -pinene (2), β -pinene (3), terpinolene (4), α -terpinene (5), α -terpineol (6), nerol (7) and linalool (8) with benzaldehyde (9) in the presence of HPW/SiO₂.

when it was necessary. The absence of the additional substrate conversion indicated the absence of the significant leaching of active components.

The products were separated by a column chromatography (silica gel 60) using mixtures of hexane and CH₂Cl₂ as eluents and identified by GC–MS, ¹H, and ¹³C NMR. The assignment of ¹H and ¹³C NMR signals were performed based on the results of bidimensional NMR methods. NMR spectra were obtained in CDCl₃ solutions on a Bruker 400 MHz spectrometer. TMS was used as the internal standard. Mass spectra were recorded on a Shimadzu QP2010-PLUS spectrometer (70 eV).

Compound 10: MS (70 eV, EI): m/z 242 (0.5) [M⁺], 136 (60%), 121 (12%), 93 (100%), 92 (50%), 91 (20%), 77 (11%). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS), δ =0.78 (s, 3H; C⁷H₃), 1.26 (s, 3H; C¹⁰H₃), 1.32 (s, 3H; C⁹H₃), 1.48 (br.s., 1H; C⁴H), 1.66 (br.d, ²J=12.4 Hz, 1H; C⁵HH), 2.06 (br.d, ²J=18.8 Hz, 1H; C³HH), 2.13 (br.s, 1H; C⁶H), 2.28 (br.d, ²J=12.4 Hz, 1H; C⁵HH), 2.33 (br.d, ²J=18.8 Hz, 1H; C³HH), 4.81 (br.s, 1H; C¹¹H), 5.37 (br.s, 1H; C²H), 7.11 (t, ³J=7.2 Hz, 1H; C¹⁵H), 7.19 (t, ³J=7.2 Hz, 2H; C¹⁴H and C¹⁶H), 7.25 ppm (t, ³J=7.2 Hz, 2H; C¹³H and C¹⁷H). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS), δ =22.97 (C⁹), 23.05 (C⁷), 26.70 (C³), 27.35 (C⁵), 27.67 (C¹⁰), 32.99 (C⁴), 40.54 (C⁶), 73.20 (C¹¹), 74.31 (C⁸), 122.28 (C²), 124.67 (C¹³ and C¹⁷), 125.52 (C¹⁵), 126.81 (C¹⁴ and C¹⁶), 132.19 (C¹), 141.91 ppm (C¹²). For atom numbering see Scheme 3. Compound 10 was reported previously [15].

Compound 11: MS (70 eV, EI): m/z 136 (12%), 121 (20%), 107 (25%), 94 (20%), 93 (30%), 92 (15%), 68 (100%), 67 (30%). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS), δ =1.37 (s, 3H; C¹⁰H₃), 1.40 (s, 3H; C⁸H₃), 2.10–2.20 (m, 1H; C⁶H), 4.40–4.45 (m, 1H; C¹¹H), 4.57 (d, ²J=15.2 Hz, 2H; C⁹H₂), 5.15–5.30 (m, 2H; C¹H₂), 5.90–6.00 ppm (m, 1H; C²H). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS), δ =22.00 (C⁸), 28.50 (C¹⁰), 51.93 (C⁶), 76.91 (C³), 79.58 (C¹¹), 113.20 (C⁹), 116.36 (C¹), 142.94 (C²), 147.47 ppm (C⁷). For atom numbering see Scheme 2. Compound 11 was isolated in a mixture with 10 in a rel-

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