

Heteropoly Acids as Versatile Catalysts for the Synthesis of Fragrances from Terpenes

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Introduction

Mono and sesquiterpenes are abundant renewable feedstock for the flavor and fragrance industry [1]. Major terpene sources are essential oils and natural resins as well as by-products of lemon and orange juice production and pulp and paper industries. Various terpenoids used in the fine chemicals industry are produced by acid-catalyzed transformations of more abundant precursors. In these reactions, mineral acids are often used as catalysts in overstoichiometric amounts to generate large amounts of waste.

Heteropoly acids (HPAs) have attracted much interest as catalysts for clean synthesis of fine and specialty chemicals [2]. Due to their strong acidity, HPAs generally exhibit higher catalytic activities than conventional acid catalysts, offering substantial economic and environmental advantages. For several years, we have been interested in the application of heteropoly acids as catalysts in various reactions of terpenoids, such as hydration, acetoxylation, and isomerization [3-6] in homogeneous and heterogeneous systems. Here, we will present our recent results, mainly focusing on heterogeneous catalysis by H₃PW₁₂O₄₀ (PW), the strongest HPA in the Keggin series.

Materials and Methods

The HPA catalysts were prepared as described elsewhere [3-6] and thoroughly characterized regarding their texture, acidity and stability. The reactions discussed were carried out in the liquid phase under mild conditions in the temperature range of 20-100 °C.

Results and Discussion

Silica-supported PW (20 wt%) is an efficient heterogeneous catalyst for the liquid-phase isomerization of various terpenic compounds, such as α -pinene, α -pinene oxide, longifolene, and α -terpineol, into more valuable isomers. For example, α -pinene and longifolene can be converted into camphene and isolongifolene, respectively, which are intermediates in the synthesis of valuable fragrances. These two reactions occur under solvent-free conditions in the temperature range of 80-100 °C, with low catalyst loadings (0.15 – 5 wt%) and high turnover numbers (up to 6000 per proton). The isomerization of α -terpineol in cyclohexane solutions yields 1,8-cineole and 1,4-cineole in good yields. Both products are useful for flavoring and pharmaceutical applications.

PW/SiO₂ also catalyzes the liquid-phase cyclization of (+)-citronellal under mild conditions giving (-)-isopulegol, an intermediate for the synthesis of (-)-menthol, in high yield. With the use of bifunctional catalyst Pd-PW/SiO₂, (+)-citronellal can be converted to menthol in one-pot process via acid-catalyzed cyclization followed by Pd-catalyzed hydrogenation, with 92% yield of menthol at 100% citronellal conversion and 85% stereoselectivity to the desired (-)-menthol. The reaction occurs in cyclohexane solution at 70 °C and 35 bar H₂ pressure, without PW and Pd leaching.

The liquid-phase hydration and acetoxylation of either limonene, β -pinene, or α -pinene catalyzed by dissolved or silica-supported PW in acetic acid and acetic acid/water solutions give α -terpineol, one of the top 30 flavor compounds, along with α -terpenyl acetate. Another monoterpene, camphene, can be selectively converted under similar conditions into isoborneol and its acetate, that are used in the formulations of soap and cosmetic perfumes and medicines, as well as in the industrial production of synthetic camphor.

A remarkable effect of the solvent nature on the catalytic performance of PW allows to direct the transformation of α -pinene oxide to either campholenic aldehyde, *trans*-carveol, *trans*-sobrerol, or pinol, and obtain each of these valuable fragrance compounds in good to excellent yields using an appropriate solvent. Solvent polarity and basicity strongly affect the reaction pathways. Non-polar non-basic solvents favor the formation of campholenic aldehyde, whereas in polar basic solvents *trans*-carveol is formed. In polar weakly basic solvents the major products are *trans*-sobrerol or pinol. On the other hand, in non-polar basic solvents, both campholenic aldehyde and *trans*-carveol are formed in comparable amounts.

Significance

We have found that silica-supported or dissolved HPA is an efficient and environment friendly acid catalyst for liquid-phase transformations of various terpenic compounds. Our synthetic protocols use renewable feedstocks and provide simple and clean routes to valuable ingredients and intermediates for the fragrance and pharmaceutical industries. In the processes studied, HPA catalysts show higher catalytic activities and selectivities than the conventional acid catalysts such as H₂SO₄ and Amberlyst-15. In many cases, the HPA catalysts can be recovered and reused.

References

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