

Synthesis of 1,8-cineole and 1,4-cineole by isomerization of α -terpineol catalyzed by heteropoly acid

Enio J. Leão Lana^a, Kelly A. da Silva Rocha^a, Ivan V. Kozhevnikov^b, Elena V. Gusevskaya^{a,*}

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

^b Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

Received 26 April 2006; received in revised form 25 May 2006; accepted 26 May 2006

Available online 18 July 2006

Abstract

The isomerization of α -terpineol (**1**) catalyzed by heteropoly acid $H_3PW_{12}O_{40}$ (PW) in homogeneous and heterogeneous systems yields 1,8-cineole (**2**) and 1,4-cineole (**3**), both useful for flavoring and pharmaceutical applications. In the homogeneous system, **2** and **3** were obtained with 25% and 23–27% selectivity, respectively, at 50–90% α -terpineol conversion (in a nitrobenzene solution, 40 °C). In the heterogeneous system, 35% of **2** and 25% of **3** were obtained at 70–100% conversion in a cyclohexane solution at 60 °C using silica-supported PW as a solid acid catalyst, and the catalyst could be recycled. PW showed a higher catalytic activity and selectivity than conventional acid catalysts such as H_2SO_4 and Amberlyst-15.

© 2006 Elsevier B.V. All rights reserved.

Keywords: 1,4-Cineole; 1,8-Cineole; α -Terpineol; Heteropoly acid; Catalysis

1. Introduction

The cineoles, possessing important biological activities, are volatile, symmetrical monoterpenic cyclic ethers. These are commonly found as components of essential oils from aromatic plants [1–6]. 1,8-cineole (1,8-epoxy-*p*-menthane also known as Eucalyptol) has a characteristic fresh and camphoraceous fragrance and pungent taste. It finds various uses as aroma and pharmaceutical chemical, e.g., as a food flavoring agent, for treating symptoms of airway diseases and in aromatherapy as a skin stimulant [7–11]. Although, 1,8-cineole is traditionally more desirable and more abundant isomer, 1,4-cineole (1,4-epoxy-*p*-menthane) is also a widely distributed natural oxygenated monoterpene found in the same plant species, however usually in much lower concentrations than 1,8-cineole. Recently, the synthetic utility of 1,4-cineole has been recognized, e.g., as a valuable intermediate for the preparation of herbicides [12]. It should also be mentioned that both cineoles have important phytotoxic properties which could render them various practical applications [13].

Cineoles can be prepared synthetically by treatment of terpene fractions or isoprene with mineral acids, usually sulfuric acid [14–16]. The rearrangements of terpineols and terpin hydrate catalyzed by mineral acids is a known procedure for making cineoles, however the relevant information is scarce [17,18]. These methods use very large amounts of mineral acids per substrate and result in complex mixtures containing relatively low amounts of 1,4- and 1,8-cineole, along with other products such as menthadienes, cymenes and terpinenes. Usually, the amount of 1,8-cineole in the final mixtures does not exceed 15%, with 1,4-cineole \leq 35%. There is a serious environmental concern about these methods due to the formation of large amount of waste. Hence, the development of a clean synthesis of cineoles is a challenging task.

Heteropoly acids (HPAs) have attracted much interest as the catalysts for clean synthesis of fine and specialty chemicals in homogeneous and especially heterogeneous systems [19–21]. Recently, HPAs have been reported as efficient catalysts for various reactions of terpenes and their derivatives such as hydration and acetoxylation [22,23], cyclization [24] and isomerization [25].

Here we report the application of heteropoly acid $H_3PW_{12}O_{40}$ (PW), the strongest HPA in the Keggin series, as homogeneous and solid acid catalysts for the isomerization of

* Corresponding author. Tel.: +55 31 3499 57 41; fax: +55 31 3 499 57 00.
E-mail address: elena@ufmg.br (E.V. Gusevskaya).

α -terpineol (**1**) to 1,8-cineole (**2**) and 1,4-cineole (**3**). To our knowledge, no attempt to use HPA as well as any other solid acid catalyst for this reaction has been made so far.

2. Experimental

2.1. Chemicals

H₃PW₁₂O₄₀ hydrate and optically pure (*R*)- α -terpineol and were purchased from Aldrich and used as received. Nitrobenzene was purified prior to use, as described elsewhere [26].

2.2. Catalyst preparation

The silica-supported HPA catalysts, H₃PW₁₂O₄₀/SiO₂ (PW/SiO₂) containing 20 and 40 wt.% PW, were prepared by impregnating Aerosil 300 (S_{BET}, 300 m² g⁻¹) with an aqueous PW solution and calcined at 150 °C/0.5 Torr for 1.5 h, as described elsewhere [27]. The PW content was confirmed by ICP. The integrity of the Keggin structure of PW was proved by ³¹P MAS NMR; the catalysts showed only a single peak at ca. -15 ppm characteristic of H₃PW₁₂O₄₀ [19,20]. The 20% PW/SiO₂ and 840% PW/SiO₂ catalysts had a BET surface area of 205 and 143 m² g⁻¹ and a pore volume of 0.74 and 0.39 cm³ g⁻¹, respectively.

2.3. Isomerization of α -terpineol

The reaction was carried out in a glass reactor equipped with a magnetic stirrer at 25–60 °C. In a typical run in homogeneous systems, a solution of α -terpineol (0.15 mol/L), dodecane (0.10 mol/L, internal standard) and PW (0.25–5.0 mol%

based on **1**) in a solvent (5.0 mL) was stirred under air at a specified temperature. In heterogeneous systems, the reaction was carried out similarly except the solid PW/SiO₂ catalyst (0.65–1.25 wt.%, based on the total amounts of the reaction mixture) and cyclohexane as a solvent were used. The reaction progress was followed by gas chromatography (GC) using a Shimadzu 17 instrument fitted with a Carbowax 20 M capillary column and a flame ionization detector. At appropriate time intervals, aliquots were taken and analyzed by GC. The GC mass balance was based on the substrate charged. The difference was attributed to the formation of oligomers, which were not detectable by GC. The products were identified by ¹H and ¹³C NMR spectroscopy (Bruker DRX-400, tetramethylsilane, CDCl₃), GC–MS on a Hewlett-Packard MSD 5890/Series II instrument operated at 70 eV and IR (Mattson FTIR 3000/Galaxy Series). The structures of all products except 1,4-cineole were also confirmed by GC using authentic samples. 1,4-Cineole was identified in the mixtures isolated after the reaction in acetone, in which 1,4-cineole was the main product (Table 1).

3. Results and discussion

3.1. Homogeneous isomerization of α -terpineol

The acid-catalyzed transformations of α -terpineol (**1**) in the presence of PW in solution were found to yield a complex mixture of products including **2** and **3** together with limonene (**4**), α -terpinene (**5**) and γ -terpinene (**6**), as well as unidentified oligomeric products (Table 1). The reaction is likely to occur via a carbenium-ion mechanism, which may be represented by Scheme 1.

Table 1
Isomerization of α -terpineol (0.15 mol/L) catalyzed by H₃PW₁₂O₄₀

Run	Solvent	Catalyst (mol%)	<i>T</i> (°C)	Time (h)	Conversion (%)	Selectivity ^a (%)					
						2	3	4	5	6	Others ^b
1	PhNO ₂	None	25	5	0	–	–	–	–	–	–
2	PhNO ₂	0.25	25	20	37	23	18	12	9	–	38
3	PhNO ₂	0.25	40	2	48	25	27	19	16	–	13
4	PhNO ₂	0.25	40	5	90	25	23	13	21	6	12
5	PhNO ₂	0.5	40	1	54	25	25	14	16	5	15
6	PhNO ₂	0.5	40	5	97	23	15	–	24	9	29
7 ^c	PhNO ₂	0.5	40	2	47	27	30	22	20	–	1
8 ^c	PhNO ₂	0.5	40	5	100	22	15	–	27	10	26
9	PhNO ₂	0.5	60	0.5	100	16	16	4.0	29	10	25
10 ^{d,e}	PhNO ₂	0.37	40	5	5	–	–	–	–	–	–
11 ^d	PhNO ₂	30	40	0.5	100	13	16	7	25	8	31
12	MeCN	0.25	40	5	0	–	–	–	–	–	–
13	MeCN	5.0	40	5	0	–	–	–	–	–	–
14	DMF	1.0	40	5	0	–	–	–	–	–	–
15	Dioxane	1.0	40	5	14	–	21	26	–	–	53
16	Acetone	0.5	40	4	28	–	46	29	9	9	7
17	Acetone	1.0	40	6	58	–	41	26	9	9	15

^a Selectivity and conversion determined by GC.

^b Mainly oligomerization products.

^c 0.5 wt.% of H₂O added.

^d H₂SO₄ as a catalyst.

^e Only traces of products detected by GC.

Download English Version:

<https://daneshyari.com/en/article/68428>

Download Persian Version:

<https://daneshyari.com/article/68428>

[Daneshyari.com](https://daneshyari.com)