

# Hydration and acetoxylation of camphene catalyzed by heteropoly acid

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## Abstract

The liquid-phase acetoxylation and acetoxylation/hydration of camphene (**1**) in homogeneous or heterogeneous systems catalyzed by dissolved or silica-supported heteropoly acid  $H_3PW_{12}O_{40}$  (PW) in AcOH/H<sub>2</sub>O solutions (0–10 vol.% H<sub>2</sub>O) have been studied. Isobornyl acetate (**2a**) and isoborneol (**3a**) are the main reaction products which have been obtained with an almost 100% total selectivity. No oligomerization of camphene has been observed. PW shows a much higher catalytic activity than conventional acid catalysts such as H<sub>2</sub>SO<sub>4</sub> and Amberlyst-15. It can be recovered without neutralization and reused.

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## 1. Introduction

Naturally occurring monoterpenes are widely used for the production of flavors and fragrances [1,2]. Previously we have reported that a number of oxygenated derivatives of monoterpenes can be obtained in good yields and, in some of the cases, with high stereoselectivity by catalytic oxidation or carbonylation of monoterpenes such as limonene,  $\beta$ -pinene, camphene and myrcene [3–8]. Acid catalyzed hydration and acetoxylation of terpenes are also important synthetic routes to valuable terpenic alcohols and esters with many applications in perfumery and pharmaceutical industry [1]. Thus, camphene is converted to borneol, isoborneol and their acetates that are used in the formulations of soap, cosmetic perfumes and medicines,

as well as in the industrial production of synthetic camphor [1]. Strong mineral acids (e.g. H<sub>2</sub>SO<sub>4</sub>) are frequently used for the hydration and acetoxylation of terpenes [1]. However, the equilibrium of camphene hydration is essentially shifted towards the camphene [9,10]. The hydration and acetoxylation of camphene are usually complicated by the formation of various by-products, such as camphene hydrate [1]. In addition, the disposal of mineral acids poses a serious environmental problem. Solid acid catalysts such as zeolites [11,12] and cation exchange resins [13–15] have also been used for the hydration of camphene. These may lead to more environmentally benign processes.

Heteropoly acids (HPAs) of the Keggin series are promising acid catalysts for the synthesis of fine and specialty chemicals [16–19]. They are employed as catalysts for the liquid-phase hydration of olefins in industry [19] and have been used for the olefin acetoxylation [20–22]. Being stronger acids, HPAs generally

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exhibit higher catalytic activities than conventional catalysts, such as mineral acids, ion-exchange resins, zeolites, etc. in both heterogeneous and homogeneous systems [16]. Furthermore, HPA catalysis lacks side reactions, such as sulfonation, chlorination, etc. that frequently occur with mineral acids. HPAs are soluble in water and polar organic solvents, such as lower alcohols and carboxylic acids, but insoluble in hydrocarbons. This provides an opportunity for the easy recovery of HPA catalysts from liquid-phase reaction systems without neutralization simply by precipitating with a hydrocarbon solvent [16]. Recently, using an HPA catalyst, we have developed an efficient method for the hydration/acetoxylation of limonene,  $\alpha$ - and  $\beta$ -pinene into  $\alpha$ -terpineol and its acetate [22], the latter being one of the top 30 commonly used flavor compounds. HPA catalysts have been successfully applied for the hydration and/or alkoxylation of camphene in aqueous organic media or in alcohol solutions [9,10,23,24]. To the best of our knowledge, no acetoxylation of camphene with HPA has been reported so far.

This work describes the application of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (PW), the strongest HPA in the Keggin series [16], as a catalyst for the liquid-phase acetoxylation and acetoxylation/hydration of camphene (**1**). Both homogeneous and heterogeneous systems are studied. Emphasis is put on achieving high selectivities towards the desired products, isobornyl acetate (**2a**) and isborneol (**3a**), by optimizing the reaction variables, such as catalyst concentration, temperature and solvent composition. Efficient methods of converting **1** into **2a** or a mixture of **2a** and **3a** are reported.

## 2. Experimental

All chemicals were purchased from commercial sources and used as received, unless otherwise stated. Camphene was distilled before use.  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$  was from Aldrich. The silica-supported catalyst, 20 wt.%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$  (PW/SiO<sub>2</sub>), was prepared by impregnating Aerosil 200 (Degussa) with an aqueous PW solution and dried at 130 °C per 0.5 Torr for 1.5 h, as described elsewhere [21]. The BET surface area of the catalyst was 174 m<sup>2</sup> g<sup>-1</sup>. The integrity of Keggin structure of PW in the fresh and used catalysts was confirmed by <sup>31</sup>P MAS-NMR;

both catalysts showed only a single peak at ca. -15.0 ppm (referenced to 85%  $\text{H}_3\text{PO}_4$ ) characteristic of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  [16].

The reactions were carried out in a glass reactor equipped with a magnetic stirrer. The homogeneous reactions were performed by adding camphene (0.3 M) to a 0.0001–0.009 M  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  solution in neat acetic acid or in an AcOH/H<sub>2</sub>O mixture pre-thermostatted at 15–60 °C. At appropriate time intervals, aliquots were taken, diluted ten-fold with hexane to precipitate the HPA and analyzed by GC using a Shimadzu 14B gas chromatograph fitted with a Carbowax 20M capillary column and a flame ionization detector. Dodecane was used as an internal standard. The products were identified by GC-MS on a Hewlett-Packard MSD 5890/Series II instrument operating at 70 eV. The heterogeneous acetoxylations were performed similarly by reacting 2.0 g of a camphene/AcOH mixture (1/1.2 (mol/mol)) with 0.025–0.100 g of 20% PW/SiO<sub>2</sub> at 40 °C for 3–4 h with intense stirring. After the reaction, the catalyst was filtered off, washed with hexane and reused. In order to prevent the leaching of PW from the catalyst the camphene/AcOH molar ratio was chosen higher than 1/3 [21]. At higher concentrations of acetic acid, some PW leaching was observed. For this reason, contact of the catalyst with neat acetic acid must be avoided. To control the leaching, diluting the filtered mixture with hexane (ca. 5-fold) was used as a test. Appearance of a white PW precipitate indicated a significant PW leaching. The GC mass balance typically made up ~100% in homogeneous reactions and 90–95% in heterogeneous reactions based on the substrate charged. The difference, 5–10%, was attributed to the formation of oligomers, which were not GC determinable and estimated semiquantitatively. In heterogeneous systems, the oligomers adsorbed on the catalyst surface were determined from the difference in the catalyst weight before and after use.

## 3. Results and discussion

### 3.1. Homogeneous system

In the presence of dissolved PW, acetic acid readily adds to camphene yielding almost exclusively isobornyl acetate (**2a**) (Table 1, runs 1–7). Only traces

Table 1  
Homogeneous acetoxylation/hydration of camphene catalyzed by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ <sup>a</sup>

Run	[PW] × 10 <sup>3</sup> (M)	T (°C)	Time (min)	Conversion <sup>b</sup> (%)	Selectivity (%)		
					2a	2b	3a
AcOH <sup>c</sup>							
1	0.1	25	60	17 (2.8)	99		<sup>e</sup>
			270	56	97		3
2	0.3	25	60	52 (2.9)	97		3
			180	90	98		2
3	0.6	25	60	90 (2.5)	99		<sup>e</sup>
			130	98	100		
4	3	25	15	85	100		
			80	98	100		
5	6	25	15	91	100		
			60	97	100		
6	3	15	40	87	100		
			80	94	100		
7	3	40	10	95	100		
8 <sup>d</sup>	72	25	60	60 (0.02)	100		
			120	73	100		
AcOH/H <sub>2</sub> O = 95/5 (v/v) <sup>c</sup>							
9	6	25	95	40	57	15	28
			215	63	66	5	29
			250	67	68	4	28
10	9	25	280	84	77		23
11	6	40	90	80	99	<sup>e</sup>	<sup>e</sup>
			200	90	99	<sup>e</sup>	<sup>e</sup>
12	3	40	90	66	93	7	
			220	86	100		
AcOH/H <sub>2</sub> O = 90/10 (v/v) <sup>c</sup>							
13	6	25	185	21	66	33	
14	6	40	60	50	50	12	38
			140	77	65		35
15	6	60	30	60	57	5	38
			110	86	77	3	19

<sup>a</sup> PW is  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ; [Camphene] = 0.3 M, conversion and selectivity were determined by GC.

<sup>b</sup> In brackets is turnover frequency ( $\text{min}^{-1}$ ) per proton in the catalyst.

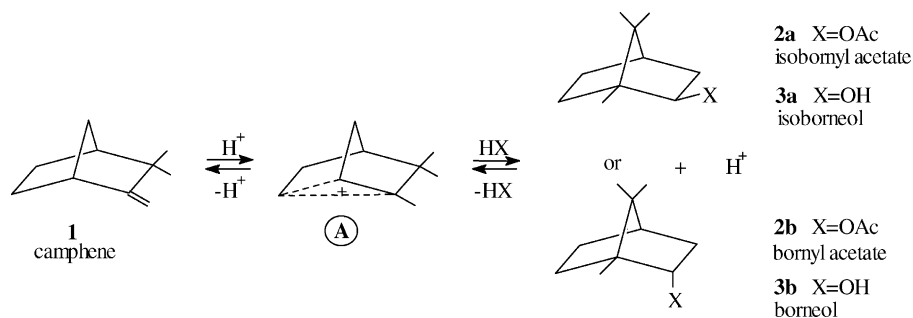
<sup>c</sup> Solvent.

<sup>d</sup> Catalyst:  $\text{H}_2\text{SO}_4$ .

<sup>e</sup> Traces of product formed.

of isorneol (**3a**) were detected despite the reaction mixture contained a small amount of water (added with the PW hydrate). In contrast to the PW-catalyzed acetylation of limonene,  $\alpha$ - and  $\beta$ -pinene [22], the acetoxylation of camphene was not complicated

by oligomerization and isomerization. Remarkably, a very high stereoselectivity was observed in this reaction—only exo-isomer **2a** was formed, without even traces of endo-isomer **2b** (Scheme 1). PW at a very low concentration ( $10^{-4}$  M) is efficient in



Scheme 1.

camphene acetoxylation at room temperature, the catalyst turnover number (per one  $\text{H}^+$  in PW) being up to 560 and substrate conversion of 56% in 270 min (run 1). At higher catalyst concentration, a virtually complete conversion of camphene was achieved in 60–180 min, with a turnover frequency (TOF) up to  $3 \text{ min}^{-1}$  (runs 2–5).

As can be seen from the data for 60 min in runs 1–3, the conversion of camphene depends almost linearly on [PW] (i.e. TOF nearly constant). Thus, the reaction is approximately first order in the catalyst. At higher PW concentrations (runs 4 and 5), the reaction was too fast for its rate to be measured accurately. An increase in temperature from 15 to  $40^\circ\text{C}$  (runs 4–6) accelerated the reaction, as expected without impairing its selectivity. In contrast to other monoterpenes [22], no oligomerization of camphene was observed even at  $40^\circ\text{C}$ .

The catalytic activity of PW (TOF) in acetoxylation of camphene is more than 100 times higher than that of  $\text{H}_2\text{SO}_4$  (cf. runs 1 and 8). This is in accordance with the higher acid strengths of PW ( $\text{p}K_1$  is 4.8 for PW and 7.0 for  $\text{H}_2\text{SO}_4$  in acetic acid [25]).

In aqueous acetic acid containing 5–10 vol.% of water, hydration competes with acetoxylation, resulting in direct formation of isoborneol (**3a**) together with isobornyl acetate (**2a**; Table 1, runs 9–15). It should be noted that isoborneol, a valuable terpenic alcohol, is usually made by the hydrolysis of isobornyl acetate. The camphene conversion decreases significantly as water content increases. The selectivity to isoborneol depends on reaction temperature and on the concentration of both PW and water, reaching 38% (runs 14, 15). Interestingly, in the presence of water at  $25^\circ\text{C}$ , bornyl acetate **2b** (endo product) formed in

significant amounts (runs 9, 13) but no borneol (**3b**) was found.

The HPA catalyst can be recovered from neat or aqueous acetic acid solutions without neutralization simply by precipitating with a hydrocarbon solvent (e.g. hexane) and, in principle, could be reused or utilized otherwise.

The HPA-catalyzed hydration/acetoxylation of camphene may be represented by Scheme 1, involving a carbenium ion mechanism, similar to that proposed for the hydration/alkoxylation of camphene elsewhere [24]. The protonation of camphene originates non-classical carbenium ion **A**, which then undergoes a nucleophilic attack by acetic acid or water to give exo or endo products **2a** and **3a** or **2b**. Apparently, all these reactions are reversible.

### 3.2. Heterogeneous system

The results on the acetoxylation of camphene with silica-supported PW are presented in Table 2. Silica is commonly used as a support for HPA; such catalysts have been reviewed elsewhere [16]. Bulk PW has been reported to exhibit a low activity in the acetoxylation of dihydromyrcene [21], which has been attributed to the small surface area of the catalyst ( $1\text{--}5 \text{ m}^2 \text{ g}^{-1}$ ) and to catalyst deactivation. Silica-supported HPA has more proton sites available for the reaction than the bulk HPA. The proton sites in PW/ $\text{SiO}_2$  are weaker than those in bulk PW due to the interaction with surface silanol groups [16] and, thus less susceptible to deactivation. The acetoxylation of camphene with 20% PW/ $\text{SiO}_2$  occurred similarly to the homogeneous acetoxylation with the formation of isobornyl acetate **2a** as the main product (95–98 mol%), small

Table 2  
Acetoxylation of camphene with solid acid catalysts at 40 °C<sup>a</sup>

Run	Catalyst (wt.%)	Time (min)	Conversion (%)	Selectivity (%)		
				2a	2b	3a
1	20% PW/SiO <sub>2</sub> (1.25)	30	9	89	3	8
		60	13	93	2	5
		120	18	96		4
2	20% PW/SiO <sub>2</sub> (2.50)	30	18	95	1	4
		60	23	96	1	3
		140	30	96		4
3	20% PW/SiO <sub>2</sub> (5.00)	10	21	93	2	5
		50	27	97		3
		120	31	98		2
4	Amberlyst-15 (1.25)	30	3	90		10
		60	5	90	5	5
		120	10	93	2	5

<sup>a</sup> Camphene/AcOH = 1/1.2 (mol/mol).

amounts of isoborneol **3a** and bornyl acetate **2b** also being formed. No significant oligomerization of camphene was observed under the conditions as shown in Table 2. The PW/SiO<sub>2</sub> catalyst, initially a white powder, turned brown during the reaction indicating catalyst blockage with carbonaceous deposit.

No leaching of HPA from the catalyst surface took place in the reaction mixture at near stoichiometric camphene/AcOH ratios. At higher concentrations of acetic acid (substrate/AcOH <1/3), some PW leaching was observed. The total concentration of the products **2a**, **2b** and **3a** in the reaction mixture reached 0.76–1.22 M (15–25 wt.%), corresponding to a 20–30% substrate conversion. In run 1 after the reaction, the catalyst was filtered off, washed with hexane and used repeatedly (three times) with ca. 10% loss of activity in each run. Thus, in the fourth run, only about half of the initial activity was observed probably because of the blockage of active sites in the catalyst by carbonaceous deposit. PW/SiO<sub>2</sub> showed a significantly higher catalytic activity than Amberlyst-15 (cf. runs 1 and 4); similar results have been obtained for the acetoxylation of dihydromyrcene [21], limonene,  $\alpha$ - and  $\beta$ -pinene [22].

#### 4. Conclusions

The liquid-phase acetoxylation and acetoxylation/hydration of camphene have been efficiently performed

in homogeneous and heterogeneous systems with the use of dissolved or silica-supported PW, the strongest HPA in the Keggin series, as the catalyst. The HPA shows a much higher catalytic activity than the conventional acid catalysts, such as H<sub>2</sub>SO<sub>4</sub> and Amberlyst-15. The valuable products, i.e. isobornyl acetate or its mixture with isoborneol (alcohol/acetate molar ratio of 4–3/6–7) have been obtained with almost 100% total selectivity. No oligomerization of camphene occurs under optimized conditions. The HPA catalyst can be recovered from acetic acid solutions without neutralization by precipitating with a hydrocarbon solvent and, in principle, could be reused.

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