

# One-pot synthesis of diisobornyl ether from camphene using heteropoly acid catalysts

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## Abstract

A novel one-pot catalytic synthesis of diisobornyl ether directly from camphene (**1**) has been developed. The reaction occurs under near ambient conditions in the presence of dissolved or silica-supported heteropoly acid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW) as a catalyst to give diisobornyl ether (**2**) with up to 90% selectivity at 50–60% conversion, along with isoborneol (**3**). Ether **2** appears to be a new compound; it was isolated as a mixture of *meso* and *dl* stereoisomers and fully characterized by MS-GC, NMR and IR spectroscopy. The supported PW catalyst can be easily separated and reused; no PW leaching from support was observed during the reaction. Conventional acid catalysts such as H<sub>2</sub>SO<sub>4</sub> or Amberlyst-15 showed no activity in this reaction.

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**Keywords:** Camphene; Etherification; Diisobornyl ether; Heteropoly acid; Catalysis

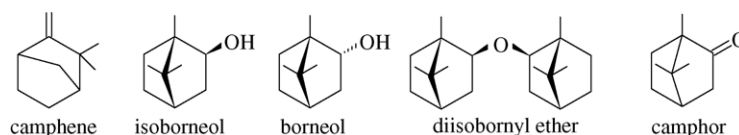
## 1. Introduction

Terpenes constitute a class of natural products that can be transformed into compounds commercially important for industrial production of fragrances, perfumes, flavors and pharmaceuticals as well as useful synthetic intermediates and chiral building blocks [1–3]. Various monoterpene esters and ethers, which are produced by acid-catalyzed reactions of monoterpenes with carboxylic acids or alcohols, respectively, can be used as fragrances. Camphene is a particularly attractive raw material employed for manufacturing synthetic substitutes for natural aromas. This compound can be converted to borneol and isoborneol as well as to their ethers and esters that are used in formulations of soap and cosmetic perfumes and medicines, as well as in the industrial production of synthetic camphor (Scheme 1) [1,4–6]. Preparation of some alkylisobornyl ethers by alkoxylation of camphene has been described [6–9], however no synthesis of diisobornyl ether, neither from isoborneol itself nor from isoborneol and camphene, has been reported yet.

Dialkyl ethers, which are widely used as octane boosters in the fuel for motor vehicles, are usually produced either by alcohol addition to olefins or by alcohol etherification. Both these reactions require strong Brønsted acid catalysts, with ion-exchange resins, such as Amberlyst-15, being a choice in industrial processes [10,11].

Heteropoly acids (HPAs), especially those of the Keggin series, are promising catalysts for the synthesis of fine and specialty chemicals [12–15]. Due to their strong acidity, they generally exhibit high catalytic activities both in homogeneous and heterogeneous systems. With HPA catalysts, no side reactions that frequently occur with mineral acids (e.g., sulfonation, chlorination, etc.) take place. HPAs are soluble in water and polar organic solvents, such as lower alcohols and carboxylic acids, but insoluble in hydrocarbons, which often allows one to recover HPA catalysts from liquid-phase reaction systems without neutralization simply by precipitating with a hydrocarbon solvent. Recently, it has been reported that homogeneous and silica-supported HPA catalysts are efficient for the hydration/acetoxylation of monoterpenes [5,16], cyclization of citronellal [17], Friedel–Crafts acylation [18] and Fries rearrangement of aryl esters [19,20]. HPAs are also active catalysts for etherification of various olefins with alcohols [4,11,21–25].

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Scheme 1.

This work describes the application of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (PW), the strongest HPA in the Keggin series, as a catalyst for the novel, one-pot conversion of camphene to diisobornyl ether, which, to our knowledge, is a new compound. Both homogeneous and heterogeneous systems are studied.

## 2. Experimental

Chemicals were purchased from commercial sources and used as received, unless otherwise stated.  $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$  and racemic camphene were from Aldrich. Benzene was purified before use, as described elsewhere [26].

$^{31}\text{P}$  MAS NMR spectra were recorded at room temperature and 4 kHz spinning rate on a Bruker Avance DSX 400 NMR spectrometer using 85%  $\text{H}_3\text{PO}_4$  as a reference. Powder X-ray diffraction (XRD) of the catalysts was measured using a Rigaku Geigerflex-3034 diffractometer with  $\text{Cu K}\alpha$  radiation. Surface area and porosity of the catalysts were measured by nitrogen physisorption at 77 K on a Micromeritics ASAP 2000 instrument. Tungsten and phosphorus content in the catalysts was measured by inductively coupled plasma (ICP) emission spectroscopy on a Spectro Ciros CCD spectrometer.

The silica-supported catalyst, 20 wt.%  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$  (PW/ $\text{SiO}_2$ ), was prepared by impregnating Aerosil 300 ( $S_{\text{BET}}$ ,  $300\text{ m}^2\text{ g}^{-1}$ ) with an aqueous PW solution and calcined at  $130\text{ }^\circ\text{C}/0.2\text{--}0.3\text{ Torr}$  for 1.5 h, as described previously [27]. The PW content was determined by ICP. The integrity of the Keggin structure of PW was confirmed by  $^{31}\text{P}$  MAS NMR; the catalysts showed only a single peak at ca.  $-15\text{ ppm}$  characteristic of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  [28]. From XRD, the catalyst included crystalline phase of PW on the silica surface. It had a BET surface area of  $200\text{ m}^2\text{ g}^{-1}$  and a pore volume of  $0.53\text{ cm}^3\text{ g}^{-1}$ .

The reactions were carried out in a glass reactor equipped with a magnetic stirrer at  $15\text{--}40\text{ }^\circ\text{C}$ . In a typical run, a mixture of camphene (0.40 M), dodecane (0.20 M, internal standard) and PW (0.5–1.0 mol% based on **1**) or solid PW/ $\text{SiO}_2$  catalyst in nitrobenzene or benzene, respectively, was intensively stirred under air at a specified temperature. 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. The GC mass balance was based on the substrate charged. The difference was attributed to the formation of oligomers, which were not GC determinable. The products were identified by GC-MS on a Hewlett-Packard MSD 5890/Series II instrument operated at 70 eV.

Catalyst recycling was performed as follows. After reaction completion, the mixture was centrifuged and the solution was taken off the catalyst with a pipette. The catalyst was washed with hexane and transferred into the reactor recharged with fresh substrate solution. To control catalyst leaching and the possibility of a homogeneous reaction, the catalyst was removed from the reaction system by centrifugation and the solution was recharged with fresh substrate and allowed to react. No conversion of camphene was observed in such experiments indicating the absence of homogeneous reaction.

Product **2** was isolated by column chromatography (silica) as a mixture (ca. 60/40) of *meso* (**2a**) and *dl* (**2b**) stereoisomers and identified by GC/MS, IR (Mattson FTIR 3000/Galaxy Series),  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Bruker DRX-400, tetramethylsilane,  $\text{CDCl}_3$ , COSY, HMQC, HMBC and DEPT experiments).

Spectroscopic data for diisobornyl ether (**2**) (light yellow oil): MS ( $m/z$ /rel. int.): 152/2, 137/44, 95/24, 81/100, 69/28, 67/30, 55/22; IR (film)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1110 [ $\nu(\text{R-O-R})$ ]. For  $^1\text{H}$  and  $^{13}\text{C}$  NMR data see Table 1.

Table 1  
NMR data for compound **2** ( $\delta$ , ppm)<sup>a</sup>

Atom	<b>2a</b> (major isomer)		<b>2b</b> (minor isomer)		HMBC (both isomers)
	$\delta$ ( $^1\text{H}$ )	$\delta$ ( $^{13}\text{C}$ )	$\delta$ ( $^1\text{H}$ )	$\delta$ ( $^{13}\text{C}$ )	
1, 1'		48.76		49.41	H-8, 8'
2, 2'	3.16–3.20 (m, 1H)	84.46	3.16–3.20 (m, 1H)	86.80	H-10, 10'; H-6, 6'; H-2', 2
3, 3'	1.52–1.55 (m, 1H) 1.67–1.70 (m, 1H)	38.48	1.57–1.67 (m, 1H) 1.70–1.76 (m, 1H)	39.79	
4, 4'	1.57–1.67 (m, 1H)	45.26	1.57–1.67 (m, 1H)	45.20	H-6, 6'; H-8, 8'
5, 5'	1.57–1.67 (m, 1H) 0.96 (m, 1H)	27.40	1.57–1.67 (m, 1H) 0.96 (m, 1H)	27.40	H-3, 3'
6 <sub>ax</sub> 6' <sub>ax</sub>	1.42–1.50 (m, 1H)	34.47	1.42–1.50 (m, 1H)	34.47	H-10, 10'; H-2, 2'
6 <sub>eq</sub> 6' <sub>eq</sub>	0.96 (m, 1H)		0.96 (m, 1H)		H-10, 10'; H-2, 2'
7, 7'		46.32		46.47	H-3, 3'; H-10, 10'
8, 8'	0.78 (s, 3H)	20.30	0.78 (s, 3H)	20.35	H-9, 9'
9, 9'	0.97 (s, 3H)	20.16	0.96 (s, 3H)	20.19	
10, 10'	0.82 (s, 3H)	12.45	0.87 (s, 3H)	12.07	H-6, 6'

<sup>a</sup> Resonance multiplicities in parentheses: s, singlet; m, multiplet.

Table 2  
Homogeneous conversion of camphene (0.40 M) catalyzed by H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW) in nitrobenzene

Run	Catalyst (mol%)	T (°C)	Time (min)	Conversion (%)	Selectivity (%)		
					2	3	Others <sup>a</sup>
1	PW (1.0)	15	30	26	87	13	
			120	51	93	2	5
			300	62	90	3	7
2	PW (1.0)	25	30	38	95	5	
			120	46	91	3	6
			300	54	90	2	8
3	PW (1.0)	40	30	38	42	4	54
			120	44	36	2	62
4 <sup>b</sup>	PW (1.0)	25	120	45	89	4	7
			150	42	88	3	9
5	PW (0.5)	25	30	25	87	5	8
			120	34	79	5	16
			300	45	71	5	24
6 <sup>c</sup>	PW (1.0)	25	30	13	0	100	
			120	22	0	100	
7	H <sub>2</sub> SO <sub>4</sub>	25	30	80	0	0	100

<sup>a</sup> Mainly, oligomerization products.

<sup>b</sup> An additional amount of camphene (0.2 M) was added to the reaction solution after 120 min.

<sup>c</sup> 0.5 wt.% of H<sub>2</sub>O was added.

### 3. Results and discussion

Transformations of camphene (**1**) in the presence of dissolved or solid silica-supported PW catalysts were studied in nitrobenzene or benzene solutions, respectively. The results obtained are presented in Tables 2 and 3. In most cases in homogeneous and heterogeneous systems, two isomers of product **2** were formed as the main products (detected by GC). Isoborneol **3** (2–6% selectivity at high conversions) was detected as a minor product. In some cases, in addition to **2** and **3**, some oligomerization products were also formed; their yield was quantified as the difference

in mass balance. Choosing appropriate reaction conditions could minimize the oligomerization.

Products **2a** and **2b** resulting from camphene were isolated from the reaction solutions as a mixture (ca. 60/40) and identified by GC-MS, IR and NMR spectroscopy. The IR spectrum of the **2a/2b** mixture shows a strong absorption at 1110 cm<sup>-1</sup>, which is characteristic of aliphatic ethers and corresponds to the asymmetric C–O–C stretching vibration [29]. From the GC-MS, IR, <sup>1</sup>H and <sup>13</sup>C NMR data, we suggest that **2** is diisobornyl ether, whose structure is shown in Scheme 1. The assignment of hydrogen and carbon resonances (Table 1), which are similar to

Table 3  
Heterogeneous conversion of camphene (0.40 M) catalyzed by H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW) in benzene

Run	Catalyst (wt.%)	T (°C)	Time (min)	Conversion (%)	Selectivity (%)		
					2	3	Others <sup>a</sup>
1	None	25	300	2	0	0	0
2	SiO <sub>2</sub> (2.0)	25	300	2	0	0	0
3	20% PW/SiO <sub>2</sub> (2.0)	25	180	19	61	34	5
4	20% PW/SiO <sub>2</sub> (2.5)	25	180	37	90	4	6
5 <sup>b,c</sup>	20% PW/SiO <sub>2</sub> (4.0)	25	180	50	90	5	5
6	20% PW/SiO <sub>2</sub> (4.0)	40	180	49	89	6	5
7	20% PW/SiO <sub>2</sub> (4.0)	60	180	36	14	3	83
8	20% PW/SiO <sub>2</sub> (4.0)	80	30	69	0	0	100
9 <sup>d</sup>	20% PW/SiO <sub>2</sub> (4.0)	25	180	0	0	0	0
			360	28	82	16	2
10	Amberlyst-15 (4.0)	25	240	15	0	11	89

<sup>a</sup> Mainly, oligomerization products.

<sup>b</sup> No conversion camphene and formation of products was observed after the catalyst was removed by centrifugation, fresh substrate added and the system allowed to react further.

<sup>c</sup> After the reaction, the catalyst was separated by centrifugation and reused three times.

<sup>d</sup> 0.5 wt.% of H<sub>2</sub>O was added.

those of isoborneol itself except for C-2 and H-2, is also supported by COSY ( $^1\text{H}$ ,  $^1\text{H}$ ), HMQC ( $^1\text{H}$ ,  $^{13}\text{C}$ ), HMBC ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and DEPT NMR experiments.

The two isomers of **2** could be *exo-exo* (diisobornyl), *exo-endo* (isobornyl-bornyl) or *endo-endo* (dibornyl) forms. The corresponding carbon and hydrogen atoms of both ring systems in each isomer show the same resonances in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, indicating that both isomers have symmetrical structures. HMBC spectra of both isomers show the long-range cross signals corresponding to the correlation between carbon C-2 and hydrogen H-2' of the other ring system. On the other hand, most of the  $^{13}\text{C}$  signals and some  $^1\text{H}$  signals (H-3, 3'; H-9, 9' and H-10, 10') for the two isomers are slightly different. The NOESY spectrum of the **2a/2b** mixture reveals that in both isomers, protons H-2/2' give NOE with protons H-6<sub>ax</sub>/6'<sub>ax</sub> showing their spatial proximity. This clearly indicates the *exo-exo* configuration for both isomers, as shown in Scheme 2. Moreover, as the chemical shifts of protons H-2 in borneol and isoborneol are significantly different ( $\Delta\delta = 0.4$  ppm [30]), this should also be expected for the corresponding ethers. However, both ring systems in **2a** and **2b** show the resonances of H-2 in the same region of 3.16–3.20 ppm (Table 1). Thus, compounds **2a** and **2b** formed from the racemic camphene are most likely to be *meso* and *dl* stereoisomers of the symmetrical diisobornyl ether (*exo-exo* configuration). Also it should be noted that only isoborneol **3** was detected by GC as byproduct. No borneol, i.e., *endo* isomer of isoborneol, was observed in detectable amounts.

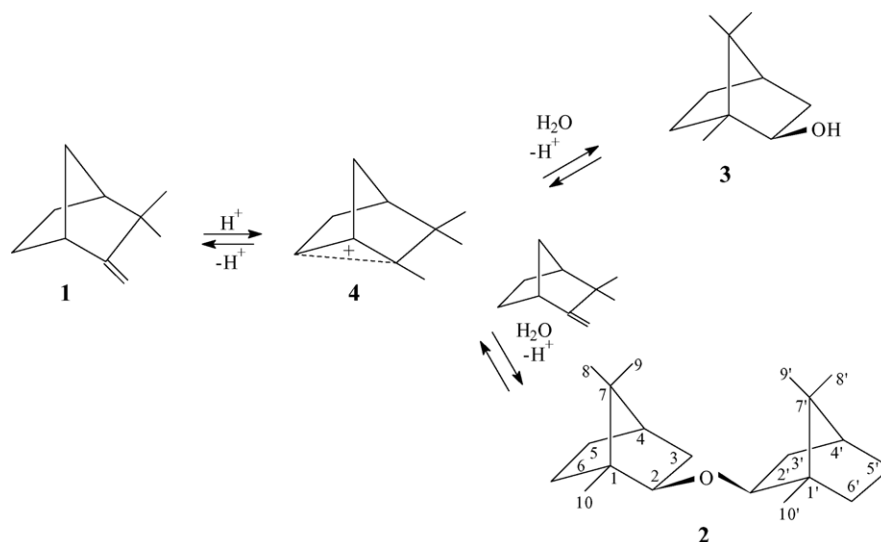
In blank reactions, with no catalyst (Table 3, run 1) or pure silica (Table 3, run 2) added, practically no camphene conversion was observed for 6 h at 25 °C in either solvent. On the other hand, PW as a homogeneous catalyst in nitrobenzene solution or silica-supported PW in benzene solution showed high activity and selectivity towards **2** under near ambient conditions. Reaction rates and selectivities depended on the conditions applied; however, in all runs, the reaction was complete in 2–3 h. The final conversions of camphene reached 40–60% depending on

the temperature, with selectivity to **2** being 90–93% under optimized conditions (Table 2, runs 1 and 2; Table 2, runs 5 and 6).

Generally, water was not added to the reaction system. The amount of hydration water present in the PW catalysts and commercial camphene was sufficient for the formation **2** and **3**. Surprisingly, the addition of only 0.5 wt.% of water to the initial reaction mixture strongly inhibited the conversion of camphene both in homogeneous (Table 2, cf. runs 2, 4 and 6) and heterogeneous (Table 3, cf. runs 9 and 5) systems. It is interesting that in the homogeneous system, differently from the heterogeneous one, the selectivity of the reaction is completely changed, with only isoborneol **3** being formed. Addition of 0.5 wt.% water to the system after reaction completion did not increase the yield of products. On the other hand, about 40% of camphene additionally added to the system was converted within 30 min (Table 2, run 4).

Thus, the role of water in this system is a complex one. We found that only traces of water are required for the reaction, whereas excess of water kills the catalyst activity. The effect of water is different in homogeneous and heterogeneous systems, which is probably related to different state of water in these systems. In homogeneous system (in nitrobenzene), water is most likely bound to HPA molecules. It should be noted that HPA crystalline hydrates could bear up to about 30 water molecules per polyanion. In heterogeneous system (2–4 wt.% of HPA/SiO<sub>2</sub> in benzene), most of water probably exists inside SiO<sub>2</sub> pores. As the SiO<sub>2</sub> porosity is about 50%, it is possible to accommodate about 1–2% water in such system with no separation of aqueous phase. This is probably the reason why water caused the different effect on the reaction selectivity in homogeneous and heterogeneous systems.

The reaction rate increased with increasing the amount of catalyst, as expected (Table 2, cf. runs 2 and 5; Table 3, cf. runs 3–5). However, the use of too small amounts of catalyst decreased the selectivity to **2** (Table 2, run 5; Table 3, run 3).



Scheme 2.

The selectivity strongly decreased when the temperature was increased to 40 °C in homogeneous systems and to 60 °C in heterogeneous systems to form high-boiling oligomers as the main products (Table 2, run 3; Table 3, run 7).

In contrast to PW, conventional acid catalysts, such as H<sub>2</sub>SO<sub>4</sub> (Table 2, run 7) or Amberlyst-15 (Table 3, run 10), showed no activity in the formation of ether **2** from camphene under similar conditions.

As PW is not soluble in benzene, no PW leaching during the reaction from the PW/SiO<sub>2</sub> catalyst was expected (Table 3, run 5). PW/SiO<sub>2</sub> is easily separable from the reaction mixture and reusable after washing with hexane. In run 5 (Table 3), 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. In homogeneous systems, PW can be recovered from nitrobenzene solutions without neutralization by precipitating with a hydrocarbon solvent and reused.

We attempted to synthesize **2** by the addition of isoborneol to camphene and by etherification of isoborneol using PW as a homogeneous catalyst in nitrobenzene or 20% PW/SiO<sub>2</sub> as a heterogeneous catalyst in benzene. Surprisingly, only dehydration of isoborneol to camphene was observed under such conditions, with no formation of ether **2**. For example, 75% of isoborneol was converted into camphene in 1 h in nitrobenzene solutions containing PW ([**1**] = [**3**] = 0.2 M; [PW] = 3.5 × 10<sup>-3</sup> M, 25 °C). In the presence of the PW/SiO<sub>2</sub> catalyst, a 30% conversion of isoborneol to camphene was observed in 4 h ([**3**] = 0.4 M; 4.0 wt.% of 20% PW/SiO<sub>2</sub>, benzene, 25 °C). No traces of **2** was found in these experiments.

Tentatively, the acid-catalyzed conversion of camphene to diisobornyl ether and isoborneol can be represented as shown in Scheme 2. The reaction involves the protonation of camphene to form non-classical carbenium ion **4**, which then undergoes a nucleophilic attack either by water to give isoborneol **3** or by camphene and water resulting in diisobornyl ether **2**. Remarkably, a very high stereoselectivity is observed in both reactions, with only *exo* isomers of the alcohol and the ether being formed. An alternative pathway via a nucleophilic attack of the initially formed isoborneol on carbenium ion **4** appears less probable because the etherification of camphene by isoborneol does not occur (see above). Many important details remain unclear, however. Why is the formation of **2** efficient when only traces of water are present in the system? Even small additives of water inhibit this reaction. No camphene dimerization to yield dicamphene is observed, although this could have been expected in the reaction system. Why is PW the effective catalyst, whereas H<sub>2</sub>SO<sub>4</sub> and Amberlyst-15 are not? Further studies are needed to answer all these questions.

#### 4. Conclusions

Diisobornyl ether was for the first time synthesized directly from camphene in liquid-phase under near ambient conditions. It was obtained with up to 90–95% selectivity at 50–60% cam-

phene conversion as a mixture of *meso* and *dl* stereoisomers. The reaction is catalyzed by dissolved or silica-supported heteropoly acid H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. No PW leaching was observed during the reaction with the supported catalyst. Both homogeneous and heterogeneous PW catalysts can be separated from the reaction mixtures and reused. Conventional acid catalysts, such as H<sub>2</sub>SO<sub>4</sub> or Amberlyst-15, showed no activity in this reaction. Attempts to synthesize diisobornyl ether by the addition of isoborneol to camphene or by the etherification of isoborneol using PW as a catalyst were unsuccessful, only dehydration of isoborneol to camphene was observed.

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