

# Dehydration of alcohols catalysed by heteropolyacids supported on silica

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Keggin type heteropolyacids supported on silica efficiently dehydrated secondary and tertiary alcohols under mild conditions and in good yields to afford the correspondent alkenes.

**Keywords:** alcohols, heteropolyacids, silica

## Introduction

Although several methods are available for the conversion of alcohols into olefins,<sup>1</sup> they involve the use of strong acids, high temperatures or transformation to ester derivatives which, in some cases, preclude their use with sensitive molecules. The synthetic utility of supported reagents has been widely demonstrated during the past 10 years.<sup>2</sup> On the other hand, the Keggin-type heteropolyacids are strong acids, particularly effective as catalysts in organic reactions occurring *via* intermediary cations. Recently we have reported the preparation of silica-supported molybdophosphoric acid and tungstophosphoric acid catalysts (MPA/S and TPA/S respectively) and showed that they were useful reagents for the dehydration of some secondary alcohols such as 1,2-diphenylethan-1-ol, 1-(3',4'-dimethoxyphenyl)-2-phenylethan-1-ol and cholesterol.<sup>3</sup>

Continuing our program of exploring the capability of these catalysts, here we extend the application of the dehydration reaction to other secondary as well as tertiary alcohols. In each of the reactions, catalysts were used several times without observing activity loss.

## Results and discussion

Here we report the use of this mild and simple novel method for the dehydration of different substituted indan-1-ols, 1,2,3,4-tetrahydronaphth-1-ols and terpenols (Tables 1 and 2).

The treatment of tertiary alcohol 1-benzyl-1,2,3,4-tetrahydronaphthol **1**<sup>7</sup> with TPA/S or MPA/S afforded the 4-benzyl-1,2-dihydronaphthalene **1a**<sup>7</sup> with excellent regio-control and yield similar to that published for the same tertiary alcohol. The 1-benzyl-6-methoxyindan-1-ol **2**, gave a mixture of the two possible alkenes 3-benzyl-5-methoxyindene **2a** and 1-(phenylmethylene)-6-methoxyindane **2b** in similar proportions. The tertiary alcohol 1,2-diphenylindan-1-ol **3**<sup>8</sup> gave the alkene derivative **3a** with quantitative yield in only 15 minutes.

With regard to the dehydration of the secondary alcohols 2-methyl-1,2,3,4-tetrahydronaphth-1-ol **4**,<sup>9</sup> 2-benzylindan-1-ol **5**<sup>8</sup> and *cis*, and *trans* 2-(3,4-dimethoxyphenyl)-5,6-dimethoxyindan-1-ol **6**, they gave the alkenes 3-methyl-1,2-dihydronaphthalene **4a**,<sup>10</sup> 2-benzylindene **5a**<sup>11</sup> and 2-(3,4-dimethoxyphenyl)-5,6-dimethoxyindene **6a**<sup>12</sup> respectively with excellent yield.

The 1,2,3,4-tetrahydronaphth-1-ol **7** and indanol **8**, both commercial compounds, afforded the corresponding alkenes 1,2-dihydronaphthalene **7a** and indene **8a**, also commercial compounds. Furthermore, in both case, the formation of the dimeric compounds **7b** and **8b**<sup>13</sup> was observed. Starting alcohols **7** and **8** were completely transformed into dimers **7b** and **8b** when heated under reflux during 3 hours and 1.5 hours respectively.

These catalysts were also useful for the dehydration and rearrangement of several terpenols.

The elimination reactions of menthol **9** and its derivatives have received extensive study.<sup>14</sup> Some of those results are presented in Table 3. It should be noted that our results with both catalysts are clearly different. Only the  $\Delta^3$ -*p*-mentene **9b** was obtained with a quantitative yield and it was characterised by <sup>1</sup>H, and <sup>13</sup>C NMR and by comparison with spectral data of the literature.

The dehydration of the secondary alcohol *iso*-borneol **10**, gave camphene **10a** when exposed to the reaction conditions during 30 min. But if the terpenol **10** was submitted to the reaction conditions during 2 hours the tricyclene **10b**<sup>15, 16</sup> was the only recovered product. The products of this reaction were monitored by CG,<sup>17</sup> and identified by <sup>1</sup>H and <sup>13</sup>C NMR.<sup>18</sup>

Finally, when the  $\alpha$ -fenchyl alcohol **11**,<sup>16</sup> was submitted to the reaction conditions in chloroform it did not result in products derived from carbocation rearrangement. However, when the solvent was changed to toluene, the tricyclic compound cyclofenchene **11a** was obtained, after 24 hours of reflux.<sup>16, 18</sup>

In short, using silica-supported heteropolyacids, the dehydration reaction of secondary and tertiary alcohols is fast and efficient. In addition, the heterogeneous conditions give clean reactions and the products are easily separated from the catalysts by a simple filtration. Products are usually given in good yield and recycling of catalysts is possible.

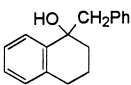
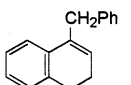
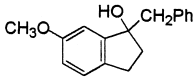
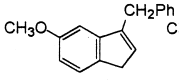
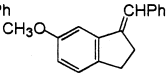
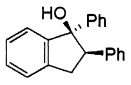
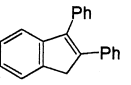
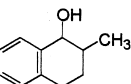
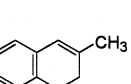
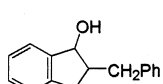
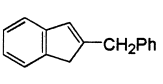
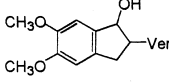
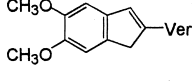


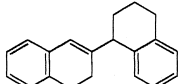


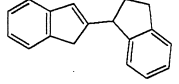
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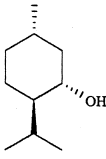
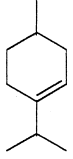
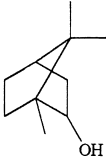
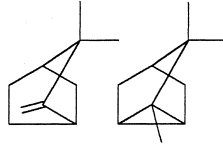
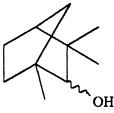
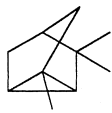
**Table 1** Dehydration of indan-1-ols and 1,2,3,4-tetrahydronaphth-1-ols catalysed by MPA/S or TPA/S

Substrate	Products	Time/min.	Yield/% (product)
 <b>1</b>	 <b>1a</b>	15	80
 <b>2</b>	 <b>2a</b>	15	55 ( <b>2a</b> ) 44 ( <b>2b</b> )
	 <b>2b</b>		
 <b>3</b>	 <b>3a</b>	15	99
 <b>4</b>	 <b>4a</b>	15	98
 <b>5</b>	 <b>5a</b>	20	99
 <b>6</b>	 <b>6a</b>	20	98
 <b>7</b>	 <b>7a</b>	15	60 ( <b>7a</b> ) 38 ( <b>7b</b> )
	 <b>7b</b>	180	
 <b>8</b>	 <b>8a</b>	20	25 ( <b>8a</b> ) 36 ( <b>8b</b> )
	 <b>8b</b>	90	

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**Table 2** Dehydration of terpenols catalysed by MPA/S or TPA/S

Substrate	Products <sup>a</sup>	Time	Yield/% (product)
 <b>9</b>	 <b>9b</b>	2 h	97
 <b>10</b>	 <b>10a</b> <b>10b</b>	30 min.	99 ( <b>10a</b> )
		2h	98 ( <b>10b</b> )
 <b>11</b>	 <b>11a</b>	24 h	97

<sup>a</sup>. Products were identified by the comparison of MS, <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of authentic samples.