



# Facile synthesis of homoallylic alcohols from aldehyde acetals in water

Dmitry E. Gremyachinskiy, Lori L. Smith, Paul H. Gross and Vyacheslav V. Samoshin\*

Department of Chemistry, University of the Pacific, Stockton, CA 95211, USA.

E-mail: vsamoshi@uop.edu

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Homoallylic and bis-homoallylic alcohols, which are widely used in organic synthesis, were prepared in good yields by a facile allylation of aldehyde acetals with allyl bromide, tin(II) chloride and potassium iodide in water.

Homoallylic alcohols are widely used in organic synthesis.<sup>1</sup> They have been prepared by a variety of methods, in particular by allylation of carbonyl compounds, mostly aldehydes.<sup>1</sup> However, some aldehydes, especially dialdehydes are unstable (e.g. malonaldehyde<sup>2</sup>), and are commercially available only in water solutions or as acetals.

To the best of our knowledge, there have been four publications describing a direct synthesis of homoallylic alcohols from acetals. Homoallylic alcohols were prepared by allylation of carbonyl compounds and some non-aromatic aldehyde acetals in water with allyldibutyltin chloride,<sup>3a</sup> and in cyclohexane/aq. LiClO<sub>4</sub> with allyl halide and Zn/Bu<sub>2</sub>SnCl<sub>2</sub>.<sup>3b</sup> A treatment with either trifluoroacetic acid or silica gel followed by tetraallyltin has been used for one-pot transformation of acetals into homoallylic alcohols.<sup>4</sup> A synthesis of homoallylic alcohols by indium mediated allylation of benzaldehyde and cinnamaldehyde dimethylacetals with allylic bromides in aqueous THF has been described recently.<sup>5</sup> Aliphatic acetals appeared to be unreactive.<sup>5</sup> Under similar conditions, *gem*-diacetates produced homoallylic acetates.<sup>6</sup> Other Lewis acid promoted reactions of acetal allylation afforded homoallylic ethers.<sup>7</sup>

We report here a mild, simple and inexpensive general synthesis of homoallylic alcohols from aldehyde acetals by treatment with allyl bromide, SnCl<sub>2</sub> and KI in water (Scheme 1, Table 1). Apparently, a hydrolysis of acetal in a weakly acidic medium preceded the allylation. These reaction conditions have been used for allylation of aldehydes,<sup>8</sup> but have never been applied to acetals.















## Experimental

### Typical procedure for acetal allylation

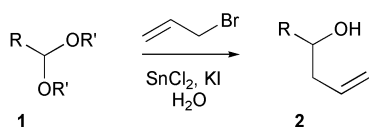
Allyl bromide (0.15 mol) was added to a mixture of SnCl<sub>2</sub>·2H<sub>2</sub>O (0.15 mol) and KI (0.15 mol) in water (200 ml). A solution of acetal **1** (0.1 mol) in THF (20 ml) was added during 1 h. The

stirring was continued for several hours (up to 48 h in case of **1f**); the acetal conversion was monitored by TLC. The resulting

**Table 1** Synthesis of homoallylic alcohols **2**

Starting acetal <b>1</b>	Homoallylic alcohol <b>2</b> <sup>a</sup>	Yield (%)
 <b>1a</b>	 <b>2a</b>	91
 <b>1b</b>	 <b>2b</b>	89
 <b>1c</b>	 <b>2c</b>	78
 <b>1d</b>	 <b>2d</b>	89
 <b>1e</b>	 <b>2e</b>	77
 <b>1f</b>	 <b>2f</b>	66
 <b>1g</b>	 <b>2g</b>	80

<sup>a</sup> All the products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass-spectrometry, and comparison with literature values: **2a**,<sup>9,10</sup> **2b**,<sup>11</sup> **2c**,<sup>12</sup> **2d**,<sup>4,8,11,13,14</sup> **2e**,<sup>15</sup> **2f**,<sup>16</sup> **2g**.<sup>17</sup>



**Scheme 1**

## Green Context

The use of water has many advantages, it is non-toxic, easy to handle, is non-inflammable and does not contribute to VOC emissions. Here, work is discussed which relates to the elaboration of aldehyde derivatives under very mild conditions. Yields are good, and the method works directly from the acetals, avoiding the often labile aldehydes themselves.

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mixture was neutralized with  $\text{Na}_2\text{CO}_3$  and was extracted with  $\text{CH}_2\text{Cl}_2$  or ether. The organic phase was washed with 5% aq.  $\text{Na}_2\text{S}_2\text{O}_3$ , and was dried and evaporated to yield a yellowish oil. The essentially pure product **2** was additionally purified by flash chromatography (silica gel; ether–hexane). In the case of **2a** and **2b**, the ether solution was concentrated on a rotary evaporator at room temperature, and the product was purified by distillation.

The amount of reagents was doubled for dialdehyde bis-acetals **1e–g**. According to NMR data, the products **2e–g** were mixtures of approximately equal amounts of diastereomers.

**1,8-Nonadien-4,6-diol (2e).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.55–1.65 (m, 2H,  $\text{CH}_2$ ), 2.25 (m, 4H,  $\text{CH}_2\text{C}=\text{C}$ ), 3.2 (br.s, 2H, OH), 3.90, 4.00 (m, 2H, CHO), 5.1–5.2 (m, 4H,  $\text{C}=\text{CH}_2$ ), 5.80 (m, 2H,  $-\text{CH}=\text{C}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  41.2, 41.4 ( $\text{CH}_2$ ), 41.9, 42.2 ( $\text{CH}_2$ ), 67.9, 71.5 (CHO), 117.4, 117.5 ( $=\text{CH}_2$ ), 134.1, 134.5 ( $-\text{CH}=\text{C}$ ).

**1,9-Decadien-4,7-diol (2f).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.45–1.75 (m, 4H,  $\text{CH}_2$ ), 2.23 (m, 4H,  $\text{CH}_2\text{C}=\text{C}$ ), 3.68 (m, 2H, CHO), 4.0 (s, 2H, OH), 5.05–5.15 (m, 4H,  $\text{C}=\text{CH}_2$ ), 5.82 (m, 2H,  $-\text{CH}=\text{C}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  32.3, 33.4 ( $\text{CH}_2$ ), 41.7, 42.0 ( $\text{CH}_2$ ), 70.8, 71.3 (CHO), 117.7 ( $=\text{CH}_2$ ), 134.9 ( $-\text{CH}=\text{C}$ ).

**1,10-Undecadien-4,8-diol (2g).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.35–1.65 (m, 6H,  $\text{CH}_2$ ), 2.2 (m, 4H,  $\text{CH}_2\text{C}=\text{C}$ ), 2.7 (br.s, 2H, OH), 3.63 (m, 2H, CHO), 5.0–5.15 (m, 4H,  $\text{C}=\text{CH}_2$ ), 5.80 (m, 2H,  $-\text{CH}=\text{C}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  21.7, 21.8 ( $\text{CH}_2$ ), 36.4, 36.6 ( $\text{CH}_2$ ), 42.0, 42.1 ( $\text{CH}_2$ ), 70.5, 70.7 (CHO), 117.6 ( $=\text{CH}_2$ ), 134.9 ( $-\text{CH}=\text{C}$ ).

This approach allows a synthesis of homoallylic and bis-homoallylic alcohols in water from readily available, stable precursors using inexpensive reagents.

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