



## HClO<sub>4</sub>-supported on silica gel: a mild and efficient catalyst for Hosomi–Sakurai reaction

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### ABSTRACT

Perchloric acid supported on silica gel was found to be an efficient catalyst (2 mol %) for the Hosomi–Sakurai allylation of numerous aldehydes with allyltrimethylsilane in the presence of benzyl alcohol. This method was also effective for the allylation of secondary alcohols under mild experimental conditions.

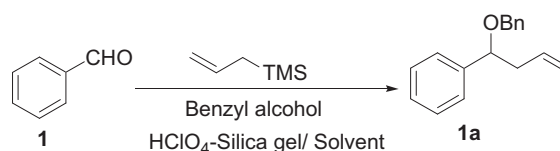
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The allylation of carbonyl compounds and acetals using allyltrimethylsilane in the presence of Lewis or Brønsted acids is called a Hosomi–Sakurai reaction,<sup>1</sup> which is an important carbon–carbon bond forming reaction in organic synthesis.<sup>2</sup> From a synthetic perspective, the allylation of acetals or ketals has been extensively explored compared to the free carbonyl compounds using Lewis acid catalysts.<sup>3</sup> However, this synthetically important transformation using Brønsted acid catalysts<sup>4</sup> has been less explored. The allylation of acetals is a useful method to generate homoallylic ethers and can be catalyzed by several Lewis acids. However, numerous acetals are not commercially available and have to be prepared from the corresponding aldehydes. In addition, most of these Hosomi–Sakurai reactions give the homoallyl alkyl ethers that require harsh conditions to be cleaved. Additionally, a direct approach prepares the homoallylic ethers from the corresponding carbonyl compounds with the silyl ether or the corresponding alcohol and an allylsilane. Catalysts that have been employed for such three-component Hosomi–Sakurai reactions using alkoxysilanes include Lewis acids such as Fe(OTf)<sub>3</sub>,<sup>5</sup> Ph<sub>2</sub>BOTf,<sup>6</sup> TMSOTf,<sup>7</sup> TMSOFs,<sup>8</sup> TMSOMs,<sup>9</sup> FeCl<sub>3</sub>,<sup>3i</sup> TMSI,<sup>10</sup> and Bi(OTf)<sub>3</sub>.<sup>11</sup> Some of these methods have potential drawbacks such as higher catalyst loading, lower yields, and longer reaction time. Furthermore, many of these catalysts are expensive, toxic, and moisture sensitive, and require stringent anhydrous reaction conditions or low temperatures.

Brønsted-acid-catalyzed direct allylation of carbonyl compounds the available method was reported by List,<sup>4i</sup> where

2,4-dinitrobenzenesulfonic acid was used as the catalyst. In the List's method, benzyl trimethyl silyl ether afforded the best results in comparison to that of benzyl alcohol together with carbonyl compounds. The continued interest in asymmetric allylation<sup>12</sup> of carbonyl compounds and the replacement of conventional Brønsted acid catalysts with more selective, acidic, and greener solid acid catalysts for various functional group transformations<sup>13</sup> leads to explore the direct allylation of carbonyl compounds. Perchloric acid supported on silica gel was found to be a promising catalyst for numerous synthetically relevant organic transformations.<sup>14</sup> The advantages of this catalyst method include high efficiency, and low-cost. Herein, this study reports the Hosomi–Sakurai allylation of aldehydes in the presence of perchloric acid supported on silica gel.

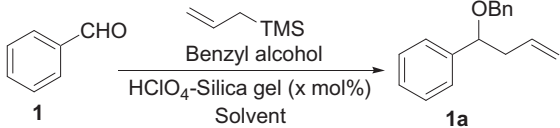
Initially, this study investigated the Hosomi–Sakurai allylation of benzaldehyde as a model substrate with allyltrimethylsilane and benzyl alcohol in the presence of silica gel supported perchloric acid (Scheme 1, Table 1). A high yield of homoallyl benzyl ether **1a** (90%) in a short reaction time was achieved in the



**Scheme 1.** HClO<sub>4</sub>-SiO<sub>2</sub>-catalyzed Hosomi–Sakurai reaction of benzaldehyde, benzyl alcohol, and allyltrimethylsilane.

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**Table 1**  
Catalyst and solvent screening


Entry	Cat (× mol %)	Solvent	Time (min)	Yield <sup>a</sup> (%)
1	2	CH <sub>3</sub> CN	30	90
2	2	DCM	240	90
3	2	Toluene	720	5
4	2	THF	720	NR
5	5	CH <sub>3</sub> CN/DCM (1:1)	10	95
6	4	CH <sub>3</sub> CN/DCM (1:1)	10	95
7	3	CH <sub>3</sub> CN/DCM (1:1)	20	96
8	2	CH <sub>3</sub> CN/DCM (1:1)	20	94
9	1	CH <sub>3</sub> CN/DCM (1:1)	30	89
10	2	CH <sub>3</sub> CN/DCM (6:4)	20	92
11	2	CH <sub>3</sub> CN/DCM (7:3)	20	97
12	2	CH <sub>3</sub> CN/DCM (8:2)	20	90

<sup>a</sup> Isolated yields.

presence of 2 equiv of benzyl alcohol in acetonitrile using a 2 mol % of the catalyst. To further optimize the reaction solvent and prevent undesired impurities, several solvents were examined. Among the various solvents employed, dichloromethane provided a better yield compared to that of acetonitrile, but required a longer reaction time for complete conversion. Only traces of product were observed in toluene, and in THF the reaction failed to occur. Surprisingly, a mixture of acetonitrile and dichloromethane (1:1) increased the product yield to 94% and lowered the reaction time (Table 1, entry 8). Further tuning of the catalyst loading and the CH<sub>3</sub>CN-DCM ratio identified (Table 1, entries 5–12) the optimal condition as a 7:3 ratio of CH<sub>3</sub>CN and DCM solvent system and a 2 mol % of the catalyst at room temperature.

Having determined the optimal experimental conditions, the HClO<sub>4</sub>-SiO<sub>2</sub>-catalyzed allylation of a broad number of aldehydes was then examined (Table 2). The reaction of isomeric tolualdehydes and 4-*tert*-butylbenzaldehyde provided the homoallyl ethers (**1b–1e**) in a high yield (entries 2 and 3). Similar results were observed from aldehydes containing electron withdrawing (halogens, NO<sub>2</sub>, CN) and releasing (OMe) groups (entries 4–9). The position of substituents on the aryl ring did not affect the yield of the reaction, as observed in the aforementioned substrates. Interestingly, cyano-substituted benzaldehydes provided the desired homoallyl ether **1p** and **1q** in good yields without the potential byproducts of hydrolysis and a Ritter reaction (entry 8).<sup>15</sup> Though methoxy substituted (*ortho* and *meta*) benzaldehydes reacted in similar to provide homoallyl ethers **1r** and **1t** in high yields, *p*-anisaldehyde provided a 1:1 mixture of the desired homoallyl ether **1s** and the diallyl derivative **3** (entry 9). All attempts to avoid the byproducts failed. Di- and trisubstituted benzaldehydes, irrespective of the nature of the substituents, were also equally effective and provided the corresponding allylated products (**1u–1w**) in good to excellent yields (entries 10–12). Compound **3** was obtained perhaps because the desired product **1s** was converted to an intermediate (**2**) and then reacted with allyltrimethylsilane to yield the product (**3**) that was ultimately obtained (Scheme 2). The diallylation did not occur in compound **1r** that might be the intramolecular hydrogen bonding between methoxy and benzyloxy groups (**4**), and inhibited the formation of compound **5**. The 3,4-dimethoxy compounds **1u** and **1v** might form the intramolecular hydrogen bonding like

**Table 2**  
The HClO<sub>4</sub>-SiO<sub>2</sub>-catalyzed allylation of aldehydes<sup>16</sup>

Entry	Product	Time (min)	Yield <sup>a</sup> (%)
1	<b>1a</b>	15	97
2	<b>1b</b> : <i>o</i> -isomer	45	90
	<b>1c</b> : <i>p</i> -isomer	30	92
	<b>1d</b> : <i>m</i> -isomer	30	88
3	<b>1e</b>	60	98
4	<b>1f</b> : <i>o</i> -isomer	30	95
	<b>1g</b> : <i>p</i> -isomer	30	98
	<b>1h</b> : <i>m</i> -isomer	30	98
5	<b>1i</b> : <i>o</i> -isomer	30	90
	<b>1j</b> : <i>p</i> -isomer	10	99
6	<b>1k</b> : <i>p</i> -isomer	20	99
	<b>1l</b> : <i>m</i> -isomer	30	98
7	<b>1m</b> : <i>o</i> -isomer	60	90
	<b>1n</b> : <i>p</i> -isomer	60	95
	<b>1o</b> : <i>m</i> -isomer	30	98
8	<b>1p</b> : <i>p</i> -isomer	30	95
	<b>1q</b> : <i>m</i> -isomer	60	90
	<b>1r</b> : <i>o</i> -isomer	30	90
9	<b>1s</b> : <i>p</i> -isomer	15	80 <sup>b</sup>
	<b>1t</b> : <i>m</i> -isomer	15	91
	<b>1t</b> : <i>m</i> -isomer	15	91
10	<b>1u</b>	10	96
11	<b>1v</b>	15	86
12	<b>1w</b>	30	70

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