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Catalytic Allylation of Hydrates of α-Keto Aldehydes and Glyoxylates with Allyltrimethylsilane Using Non-Fluorine-Containing Sulfonic Acids as Catalysts*

Ming Wen Wang, Yong Jun Chen, and Dong Wang

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China; Fax: 8610-62559373; E-mail: dwang70118@yahoo.com

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ABSTRACT: *Methanesulfonic acid, aromatic sulfonic acids, and 10-camphorsulfonic acid have been used as catalysts in allylation of hydrates of α-keto aldehydes* **1a–d** *and glyoxylates* **1e–f** *with allyltrimethylsilane* **2** *to afford the corresponding homoallylic alcohols* **4a–e** *in good yields. Two plausible mechanisms of sulfonic acid–catalyzed allylation reactions with an allysilane are discussed.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:534–538, 2001

INTRODUCTION

The allylation of carbonyl compounds with an allylsilane under Lewis acid conditions (the Hosomi-Sakurai reaction [1]) has been extensively used for the formation of carbon–carbon bonds in organic synthesis [2]. This reaction can be promoted by stoichiometric amounts of a conventional Lewis acid such as $TiCl_4$, $SnCl_4$, and $AlCl_3$ and catalyzed by various species, such as fluoride ions [3], lanthanide triflate [4], trimethylsilyl triflate (TMSOTf) [5], a superacid $TfOH_2^+$ $B(OTf)_4^-$ (prepared from BBr_3 and TfOH) [6], and a Brönsted acid $HN(SO_2F)_2$ [7]. The strong electron-withdrawing fluorine atom contained in these catalysts appears to be very important for the catalytic capability. A question arises whether reagents without a fluorine substituent could also catalyze the Hosomi-Sakurai reaction. On the other hand, since allyltrimethylsilane is likely hydrolyzed under acidic conditions [8], a Brönsted acid has been used only a few times as a catalyst for the addition of allylsilane to carbonyl compounds [7]. Herein, we wish to report the results on the allylation of aldehydes with allyltrimethylsilane (Hosomi-Sakurai reaction) catalyzed by non-fluorine-containing sulfonic acids, including methanesulfonic acid, aromatic sulfonic acids, and 10-camphorsulfonic acid.

RESULTS AND DISCUSSION

Methanesulfonic Acid as a Catalyst

The allylation reactions of hydrates of α-keto aldehydes (**1b–d**) and glyoxylates (**1e–f**) with allyltrimethylsilane **2** in the presence of a catalytic amount (10 mol %) of methanesulfonic acid (MsOH) (**3**) were carried out in dichloromethane (Scheme 1) at room temperature for a given time to afford the corresponding α-keto (**4a–c**) and α-ester (**4d,e**) homoallylic alcohols

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Correspondence to: Dong Wang.

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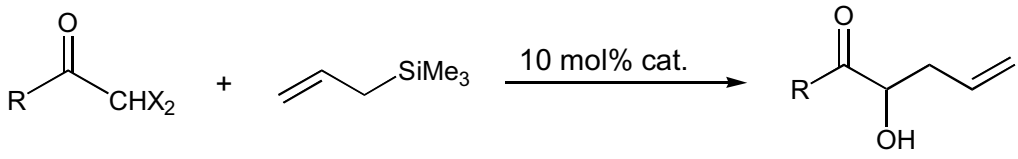
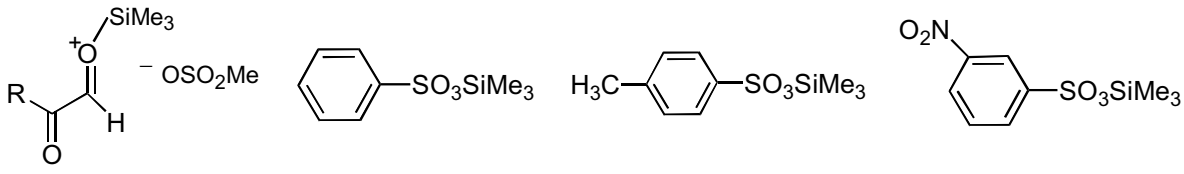


2

1a R = Ph, X_2 = O
1b R = Ph, X = OH
1c R = p-MeOPh, X = OH
1d R = p-HOPh, X = OH
1e R = BuO, X = OH
1f R = menthylO, X =OH

4a R = Ph
4b R = p-MeOPh
4c R = p-HOPh
4d R = BuO
4e R =menthylO



7 9a 9b 9c

SCHEME 1

in yields of 62–74% (Table 1). The reactions show very good chemoselectivity with the retention of keto and ester carbonyl groups. In the case of (−)-menthyl glyoxylate **1f** [9], the diastereomeric excess (de) of the product **4e** is 13%, determined by diastereomeric protons in ^{1}H NMR spectra.

With regard to the results of the MsOH-catalyzed Hosomi-Sakurai reaction, we became inquisitive as to whether MsOH would be an actual catalyst itself. When the reaction mixture of **2** and **3** is monitored by ^{1}H NMR spectroscopy, a new up-field peak at δ 0.38, assigned to silylmethyl protons of trimethylsilyl methanesulfonate (**5**, TMSOMs) ([10]: δ 0.4) appears soon, and this clearly supports the in situ formation of protodesilylation product **5** in the course of the reaction. Furthermore, the allylation reaction of **1b** with **2** using **5** as a catalyst, which was prepared by the reaction of **3** with chlorotrimethylsilane, gave **4a** in a comparable yield 65% (entry 2 vs. 1). It is interesting to note from the results that the in situ–generated TMSOMs from mixing **2** with **3** retains catalytic capability even in the case of the substrates

TABLE 1 Methanesulfonic Acid–Catalyzed Allylation of **1a–f**[a]

Entry	*Substrate*	*Catalyst*	*Amount of cat. (mol %)*	*Temp. (°C)*	*Time (h)*	*Product*	*Yield*[b] *(%)*
1	**1b**	**3**	10	25	12	**4a**	66
2	**1b**	**5**	10	25	12	**4a**	65
3	**1a**	**3**	10	25	10	**4a**	62
4	**1c**	**3**	10	25	12	**4b**	63
5	**1d**	**3**	10	25	12	**4c**	70
6	**1e**	**3**	10	25	8	**4d**	74
7	**1f**	**3**	10	25	15	**4e**	72
8	**1b**	**6**	20	40	10	**4a**	54

[a]Solvent: CH_2Cl_2.
[b]Isolated yield.

bearing active protons of a hydroxyl group. However, decomposition or deactivation of the conventional moisture-sensitive Lewis acid catalysts might occur by using the same substrates. Corresponding to aldehyde hydrate **1b**, adehyde **1a**, prepared by dehydration of **1b** by distillation under P_2O_5, has similar reactivity in the methanesulfonic acid catalyzed allylation reactions (entry 3 vs. 1). In the reaction mixture of **1b** with **2**, the formation of **1a** was observed. It is suggested that there might be an equilibrium between **1a** and **1b** in the reaction media, and the formed **1a** is activated by in situ-generated TMSOMs and reacts with **2**, driving the equilibrium to the side of the aldehyde **1a**. Thus, similar to the plausible mechanism for the TMSOTf catalyzed reaction, suggested by Davis [6b], the catalyzed allylation reaction of aldehyde hydrates with **2** in the presence of **3** could be assumed to involve the in situ generation of the oxonium cation **7** with counterion MsO^-. The catalytic function of MsOH **3** performs by producing an actual catalyst, TMSOMs.

In comparison, a catalytic amount of trifluoromethanesulfonic acid (TfOH), (**6**) [11] was used as a catalyst in the reaction of **1b** with **2**. It was found that stronger reaction conditions (reaction temperature 40°C; 20 mol % of catalyst) were required, and a relatively low yield of product (45%) was obtained.

Aromatic Sulfonic Acids as Catalysts

The reactions of α-keto aldehyde hydrate **1b** with **2** in the presence of aromatic sulfonic acids, including benzenesulfonic acid **8a**, *p*-toluenesulfonic acid **8b**, and *m*-nitrobenzenesulfonic acid **8c** were examined (Table 2). It was found that the aromatic sulfonic acids **8a–c** have a lower catalytic ability than MsOH **3** under the same reaction conditions. A higher reaction temperature (40°C) and more catalyst (20 mol %) are required. The substituents on the benzene ring, either methyl or the nitro group, do not influence the catalytic ability in the allylation reaction. Similarly, the new up-field peaks of tetramethylsilane (TMS) in the ^{1}H NMR spectra of the mixtures of **8a**, **8b**, or **8c** respectively with **2** were observed. The chemical shift at δ 0.36 is assigned to the TMS proton of trimethylsilyl benzenesulfonate **9a** ([12]: δ 0.39), that at δ 0.37 is assigned to trimethylsilyl *p*-toluenesulfonate **9b** ([12]: δ 0.38), and that at δ 0.44 is assigned to trimethylsilyl *m*-nitrobenzenesulfonate **9c**. By using **9a** as a catalyst, the allylation of **1b** proceeds smoothly giving the corresponding homoallylic alcohol **4a** in 69% yield. However, other types of organic acids, such as benzoic acid and heptanoic acid, were not effective in this reaction at all, with starting materials being recovered. The aromatic sulfonic acid–catalyzed allylation of aldehydes with **2** also seemed to be effected by the protodesilylation intermediates of **2** with sulfonic acid.

10-Camphorsulfonic Acid as a Catalyst

10-Camphorsulfonic acid (CSA), (**10**) has been used extensively in synthetic organic chemistry as an acid catalyst [13]. By using a catalytic amount of **10** (10 mol %), the reactions of **1b–f** with **2** in acetonitrile at room temperature proceeded smoothly to afford the products **4a–e** in yields of 64–78% (Table 3). The allylation of aldehyde hydrate **1a**, catalyzed by **10**, also gave **4a** in good yield (68%) (entry 1). The hydroxyl group in each substrate does not need to be protected. Even in the presence of traces of water, (CH_3CN/H_2O [50:1 to 20:1]), the CSA-catalyzed allylation reactions still proceeded smoothly (entries 3, 7, and 8). In order to examine the mechanism of the CSA-catalyzed allylation reaction, the following experiments were carried out: (1) after stirring of the mixture of **10** with **2** for 6 hours, no ^{1}H NMR peak of the corresponding TMS proton was detected, and the starting material **10** was recovered; (2) in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (15 mol %) [14], a known proton scavenger, the CAS-catalyzed allylation reaction does not proceed at all; (3) the reaction of **10** with chlorotrimethylsilane gave complicated products, but no formation of the corresponding TMSOCSA compound was detected. It is

TABLE 2 Aromatic Sulfonic Acid–Catalysed Allylation of **1b**[a]

Entry	*Catalyst*	*Amound of cat. (mol %)*	*Temp. (°C)*	*Time (h)*	*Product*	*Yield*[b] *(%)*
1	**8a**	20	40	10	**3a**	45
2	**8b**	20	40	10	**3a**	40
3	**8c**	20	40	10	**3a**	57
4	**9a**	20	40	12	**3a**	64

[a]Solvent: CH_3CN.
[b]Isolated yield.

TABLE 3 CSA-Catalyzed Allylation of **1a–g**[a]

Entry	*Substrate*	*Solvent*[b]	*Temp. (°C)*	*Time (h)*	*Product*	*Yield*[c] *(%)*
1	**1a**	A	25	10	**4a**	68
2	**1b**	A	25	10	**4a**	66
3	**1a**	B	25	10	**4a**	52
4	**1c**	A	25	10	**4b**	64
5	**1d**	A	25	10	**4c**	70
6	**1e**	A	25	6	**4d**	78
7	**1e**	B	25	6	**4d**	72
8	**1e**	C	40	6	**4d**	50
9	**1f**	A	25	8	**4e**	61

[a]Catalytic loading: 10 mol %.
[b]A:CH_3CN, B:CH_3CN/H_2O (50:1); C: CH_3CN/H_2O (20:1).
[c]Isolated yield.

confirmed that CSA does not cause protodesilylation of allylsilane to give TMSOCSA in the course of the reaction. Based on these results, the CSA-catalyzed allylation reaction seems to be through an H^+-catalysis cycle suggested by Davis [6b], and CSA functions as a Brönsted acid catalyst for the addition of allylsilane to carbonyl compounds. On the other hand, by use of (+)-**10** as a catalyst, the product of the allylation is racemic (enantiomeric excess [ee] = 0%), while for chiral glyoxylate, **1f**, the de of product **4e** is 11% in spite of a good yield 61% (entry 9). The low diastereoselectivity is reasonable with respect to the suggested H^+-catalysis mechanism.

It can be concluded from the previously mentioned investigations that the non-fluorine-containing sulfonic acids also can play a catalytic role in some Lewis acid–catalyzed reaction systems, while the presence of the strong electron-withdrawing fluorine atom is not an essential ingredient [15]. The sulfonic acids able to be employed in the catalytic Hosomi-Sakurai reaction are extremely cheap and easy to handle and may possibly be applied to other types of Lewis acid–catalyzed reactions.

EXPERIMENTAL

All the chemicals used were reagent grade. IR spectra were recorded by a Perkin-Elmer 782 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Varian XL-300 spectrometer. NMR spectra are reported in ppm with respect to TMS. Mass spectra were taken at 60 eV with an AEI MS-50/PS-30 instrument. Microanalysis was performed on a Calro 1102 Element Analysis instrument. Oxidation of the substituted acetophenones with selenium dioxide gave the hydrates of α-keto aldehydes **1b–d** [16]. The hydrate of glyoxylate **1e** was prepared according to Ref. [17], while (−)-menthyl glyoxylate **1f** was prepared according to Kornblum's method [9].

General Procedure

MsOH-Catalyzed Allylation Reaction. To a solution of **2** (1 mmol) in 1 mL of CH_2Cl_2, MsOH (0.05 mmol) was added at room temperature. After the mixture had been stirred for 1 hour, the aldehyde hydrate (0.5 mmol) was added. The mixture was stirred for a given reaction time at a given temperature, treated with brine, and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by flash chromatography on silica gel to give the corresponding homoallylic alcohol.

Aromatic Sulfonic Acid-Catalyzed Allylation Reaction. To a solution of **2** (1 mmol) in 1 mL of CH_3CN, an aromatic sulfonic acid (0.05 mmol) was added at room temperature. After the mixture had been stirred for 1 hour, aldehyde hydrate (0.5 mmol) was added. The mixture was stirred for a given reaction time at a given temperature, treated with brine, and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by flash chromatography on silica gel to give the corresponding homoallylic alcohol.

CSA-Catalyzed Allylation Reaction. To a solution of **2** (1 mmol) and aldehyde hydrate (0.5 mmol) in 1 mL of CH_3CN, CSA (0.05 mmol) was added, followed by stirring for a given reaction time at a given temperature. The reaction mixture was treated with brine and extracted with ether. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by flash chromatography on silica gel to give the corresponding homoallylic alcohol.

Compound **4a** [18]: colorless oil, IR: ν = 3442, 2900, 1670, 1588, 1440 cm^{-1}. ^1H NMR δ = 2.34–2.43 (m, 1H,), 2.68–2.74 (m, 1H), 5.02–5.20 (m, 3H), 5.76–5.87 (m, 1H), 7.51–7.95 (m, 5H). *m/z* 176 (M^+, 1.0), 135 ($M^+ - 41$, 10.7), 105 (100).

Compound **4b** [4a]: colorless oil, IR: ν = 3470, 2940, 1670, 1570, 1260, 965 cm^{-1}. ^1H NMR δ = 2.33–2.38 (m, 1H), 2.63–2.65 (m, 1H), 3.90 (s, 3H), 5.00–5.12 (m, 2H), 5.72–5.85 (m, 1H), 6.98 (d, 2H, J = 9 Hz), 7.91 (d, 2H, J = 9 Hz). *m/z* 206 (M^+, 2.5), 135 (100).

Compound **4c** [4a]: colorless oil, IR: ν = 3430, 2950, 1660, 1510, 1280, 1070, 960 cm^{-1}. ^1H NMR δ = 2.29–2.42 (m, 1H), 4.99–5.16 (m, 2H), 5.74–5.82 (m, 1H), 6.50 (s, 1H), 6.92 (d, 2H, J = 9.0 Hz), 7.88 (d, 2H, J = 9.0 Hz).

Compound **4d**: Colorless oil. IR: ν = 3480, 3070, 1760, 1635, 1460, 910 cm^{-1}. ^1H NMR δ = 0.87 (t, 3H, J = 7.3 Hz, CH_3), 1.20–1.50 (m, 2H, CH_2), 1.55–1.70 (m, 2H, CH_2), 2.18 (s, 1H, OH), 2.35–2.80 (m, 2H, CH_2), 4.12 (dt, 2H, J = 2.0, 6.6 Hz), 4.19 (dd, 1H, J = 4.8, 6.4 Hz), 5.05–5.22 (m, 2H, $=CH_2$), 5.7–5.9 (m, 1H, =CH). ^{13}C NMR δ = 13.57, 19.01, 30.57, 38.69, 65.52, 69.92, 118.58, 132.48, 174.48. Anal calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.65; H, 9.27.

Compound **4e**: Colorless oil. IR: ν = 3450 (OH), 2900, 1720 (C=O), 1620, 1210 cm^{-1}. ^1H NMR δ = 0.71–0.78 (2d, 3H, CH_3), 0.80–0.95 (m, 6H), 0.95–2.10 (m, 9H), 2.30–2.64 (m, 2H), 4.24 (dd, 1H, J = 2.0, 6.4 Hz, CH), 4.80 (dt, 1H, J = 4.6, 6.4 Hz, CH), 5.10–5.25 (m, 2H, $=CH_2$), 5.70–5.90 (m, 1H, =CH); ^{13}C NMR δ = (15.7, 16.2), (20.6, 20.8), 21.9, (22.8, 23.3), (25.8, 26.2), 31.3, 34.0, (38.6, 38.7), (40.6, 40.8), (46.8, 46.9), (69.6, 70.0), (75.9, 76.1), (118.6, 118.7), (132.3, 132.4), 174.0. The data in parentheses are from two diastereoisomers. Anal. Calcd. for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.76; H, 10.28.

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