Efficient Nucleophilic Substitution of α-Aryl Alcohols with 1,3-Dicarbonyl Compounds Catalyzed by Tin Ion-Exchanged Montmorillonite

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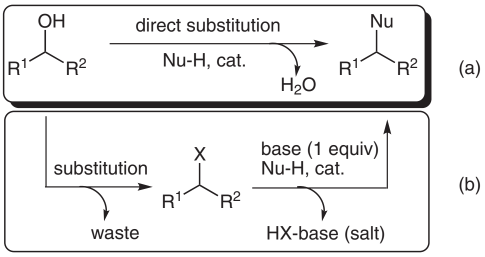
Abstract: Tin ion-exchanged montmorillonite demonstrated the high catalytic activity for the direct nucleophilic substitution of a hydroxyl group in α-aryl alcohols with various 1,3-dicarbonyl compounds including less acidic 1,3-diesters in crude solvents to afford the benzylated products accompanied by water.

Key words: tin ion-exchanged montmorillonite, heterogeneous catalysis, nucleophilic substitution, α-aryl alcohols, 1,3-dicarbonyl compounds

Benzylation at the active methylenes of 1,3-dicarbonyl compounds with α-aryl alcohols has aroused considerable interests because this protocol leads to the straightforward construction of carbon–carbon bonds. However, due to the poor leaving ability of a hydroxyl group, the alcohols are normally transformed into the corresponding halides, carbonates, or phosphates, followed by the substitution with nucleophiles. The reactions of those electrophiles having good leaving groups with typical nucleophiles require equimolar amounts of bases, thereby causing the stoichiometric production of waste salts (Scheme 1b). In light of atom economy as well as easy availability of alcohols, the direct substitution of the alcohols with nucleophiles like 1,3-dicarbonyls is a more preferable process (Scheme 1a) than the indirect one (Scheme 1b).



Scheme 1 (a) The direct substitution process of an alcohol with a nucleophile accompanied by only water; (b) and the indirect one of the alcohol involving waste salt

A variety of nucleophiles, such as indoles,[1,2] 1,3-dicarbonyls,[1,3–6] allylsilane,[7,8] amines,[9] amides,[10] trialkylsilyl cyanide,[11] enolsilane,[12] silyl ketene acetal,[12] and thiol,[13] have been found to react directly with alcohols in the presence of various catalysts. Especially for the direct substitution of alcohols with 1,3-dicarbonyl compounds, homogeneous Lewis and Brønsted acid catalysts, such as MX_n (M = Cu, Zn, Ta, Au, In, Bi, Fe, or In; X = I, Cl, Br, ClO_4 or triflate),[1,4,6,14–16] $AgSbF_6$,[6] *p*-toluenesulfonic acid,[13,17] trifluoromethanesulfonic acid,[13,17,18] heteropoly acid,[19] have been applied. However, these catalysts generally have drawbacks such as low activity, low selectivity, and difficulty in their reuse, and require long reaction times. While the direct substitution of alcohols with typical active methylenes was reported to proceed in the presence of a solid acid, proton ion-exchanged montmorillonite (H-Mont), H-Mont failed to catalyze the reaction with 1,3-diesters which have relatively higher p*K*a values of α-protons among active methylenes.[3,20] Therefore, it is still required to discover an efficient solid catalyst for the reaction of alcohols with 1,3-diesters.

Montmorillonite, a naturally occurring clay, is composed of stacked, negatively charged two-dimensional aluminosilicate layers that hold exchangeable cationic species, mostly sodium ions in the interlamellar space.[21] We have been interested in various metal ion-exchanged montmorillonites as solid acid catalysts.[22–24] Among the various metal ion-exchanged montmorillonites, tin ion-exchanged montmorillonite (Sn-Mont) was considered the most acidic for the silylation of alcohols.[23] More recently, we found that the mesoporous Sn-Mont, which was a composite of SnO_2 nanoparticles and aluminosilicate layers,[25] was completely different from those of other ion-exchanged montmorillonites, such as copper ion-exchanged montmorillonite (Cu-Mont) including monomeric copper aqua complexes[26] and iron or titanium ion-exchanged montmorillonite (Fe-Mont, Ti-Mont) intercalating chain-like iron or titanium hydroxide polymers.[27] Sn-Mont demonstrated the unique high catalytic activity for the cyanosilylation of highly congested ketones,[24] the one-pot Strecker synthesis of α-amino nitriles, especially from ketones with amines,[28] and the direct allylation of α-aryl alcohols.[8] In order to further unveil the high potential of Sn-Mont for organic synthesis, we demonstrate the usefulness of Sn-Mont for the direct substitution of alcohols with 1,3-dicarbonyl compounds, especially less acidic 1,3-diesters in the present study.[29] The detailed synthesis and characterization of Sn-Mont (Sn content: 1.9 μmol/mg; BET surface area 280 m^2g^{-1}) can be found in our previous reports.[24,28]

To begin with, the substitution of benzhydrol (**1a**, 1 mmol) with dimethyl malonate (**2a**, 1.5 mmol) in the presence of

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Sn-Mont (25 mg, 4.75 mol%) at 100 °C in 1.5 hours was selected as a model reaction to investigate solvent effects on the conversion and selectivity as shown in Figure 1. In our study, we used crude solvents without any dehydration treatment prior to use. In tetrahydrofuran was obtained only a symmetric ether **4a** derived from the self-condensation of **1a** without any desired alkylated 1,3-dimethyl ester **3aa**, while the conversion of **1a** was 70%. In 1,4-dioxane, toluene, and heptane, **3aa** was produced in unsatisfactory selectivities (8–49%) even with good conversions of 80–96%. The reaction without a solvent resulted in a moderate conversion (81%) and selectivity (74%). The obvious improvement in the conversion (97%) and the selectivity (94%) was achieved for the reaction in 1,2-dichloroethane (DCE) at 100 °C. Lower reaction temperature (80 °C) sharply decreased the selectivity of **3aa** to 66% even in DCE. Accordingly, performing the reaction in DCE at 100 °C is optimal for the substitution of alcohols in the presence of Sn-Mont.

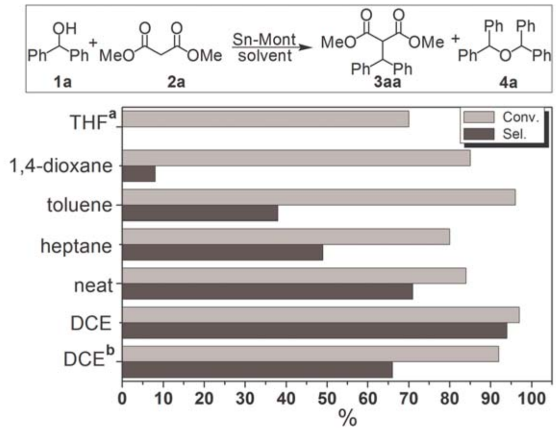


Figure 1 Solvent effects on α-diphenylmethylation of dimethyl malonate (**2a**) with **1a** catalyzed by Sn-Mont. *Reagents and conditions*: Sn-Mont (25 mg, 4.75 mol%), benzhydrol (**1a**; 1 mmol), dimethyl malonate (**2a**; 1.5 mmol), 100 °C, 1.5 h, solvent (2 mL). The conversions and selectivities were determined by GC using *n*-dodecane as an internal standard based on **1a**; the formation of bis(diphenylmethyl) ether (**4a**) accounts for the differences between the conversion of **1a** and the yield of **3aa**. [a] The reaction was conducted under reflux conditions. [b] The reaction was conducted at 80 °C.

A comparison of catalytic activity between solid acids and homogeneous Brønsted acids was conducted in the reaction of **1a** with **2a** under the optimal reaction conditions, showing the highest catalytic activity of Sn-Mont as shown in Table 1. No reaction took place in the absence of a catalyst or in the presence of Na-Mont (entries 1 and 2). Among various ion-exchanged montmorillonites, a catalytic amount of Sn-Mont (25 mg, 4.75 mol%) showed the best activity and gave a 97% conversion of **1a** and a 91% yield of **3aa** (entry 3). In contrast, other montmorillonites such as Al-Mont, Ti-Mont, Cu-Mont and commercially available K10 gave unsatisfactory yields of **3aa**, while good conversions (83–98%) of **1a** were attained in all cases (entries 3–8). Similar trends in the catalysis were also observed for the silylation of alcohols,[23] the cyanosilylation of ketones[24] and the Strecker synthesis of α-amino nitriles[28] by use of ion-exchanged montmorillonites. The reaction hardly proceeded in the presence of $Sn(OH)_4$ prepared from $SnCl_4$ with aqueous NH_3, crystalline SnO_2, and Sn- or Al-containing ordered mesoporous silica with high specific surface areas[30] (entries 9–12). The use of the proton ion-exchanged zeolites, such as H-Beta and H-Y, evidently consumed **1a**, but no **3aa** was produced (entries 13 and 14). It is surprising that homogeneous Brønsted acids, *p*-toluenesulfonic acid monohydrate (*p*-$TsOH{\cdot}H_2O$) and H_2SO_4 gave **3aa** in very poor yields of 3–5% together with large amounts of side products (entries 15 and 16), while *p*-$TsOH{\cdot}H_2O$ was reported to efficiently promote the reactions with 1,3-diketones in up to 96% yields.[13,17]

Table 1 Comparison of Different Catalysts for α-Benzylation of **2a** with **1a**[a]

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\text{DCE, 100 °C, 1.5 h}]{\text{cat.}} \mathbf{3aa}$$

Entry	Catalyst	Conversion (%)[b]	Yield (%)[b]
1	no catalyst	0	0
2	Na-Mont	0	0
3	Sn-Mont	97 (98[c])	91 (90[c])
4	Al-Mont	98	69
5	Ti-Mont	97	28[e]
6	Fe-Mont	93	19[e]
7	Cu-Mont	83	trace[e]
8	Mont K10	96	16[e]
9	$Sn(OH)_4$	0	0
10	SnO_2	0	0
11	Sn-MCM-41	0	0
12	Al-MCM-41	0	0
13	H-Beta	100	0[e]
14	H-Y	90	0[e]
15	*p*-$TsOH{\cdot}H_2O$[d]	95	0[e]
16	H_2SO_4[d]	94	0[e]

[a] Reaction conditions: catalyst (25 mg), **1a** (1 mmol), **2a** (1.5 mmol), DCE (2 mL), 100 °C, 1.5 h.

[b] Determined by GC using *n*-dodecane as an internal standard based on **1a**.

[c] The conversion and yield in parentheses were obtained for the reactions using the recovered catalyst.

[d] 5 mol%.

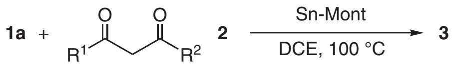
[e] The main product was **4a** in these reactions.

The high catalytic performance of Sn-Mont was also confirmed for the large-scale reaction of **1a** (10 mmol) with **2a** (15 mmol) in the presence of 50 mg of Sn-Mont in 1.5

hours. After the reaction, the used catalyst was easily separated by simple filtration from the reaction mixture, and **3aa** was obtained in a 91% isolated yield after silica gel chromatography, indicating a high turnover number (TON) of 95.8. These values are evidently an order of magnitude higher than those in the preceding studies using the homogeneous or heterogeneous catalysts such as $FeCl_3$ (8.2),[15] and $FeCl_3$–SiO_2 under microwave irradiation (9.3).[16] The recovered Sn-Mont could also be reused without any significant loss of its high catalytic performance and selectivity (Table 1, entry 3).

To further demonstrate the practical applicability of Sn-Mont, a series of 1,3-dicarbonyl compounds (**2a**–**f**) were applied to the substitution of **1a** under the optimal reaction conditions.[31] As presented in Table 2, Sn-Mont could efficiently catalyze the reactions of **1a** with not only diesters (**2a**,**b**), but also diketones (**2c**–**e**) as well as a keto ester (**2f**), and the yields in all cases were more than 90%. For the reaction of **1a** with diethyl malonate (**2b**; entry 6), the desired alkylated product **3ab** was obtained in a 93% isolated yield with a TON of 19.6. The TON is much higher than that of $InCl_3$ (12.2).[1] In sharp contrast, it was reported that the reaction of **1a** with **2b** failed in the presence of H-Mont.[20]

Table 2 Reactions of **1a** with Different 1,3-Dicarbonyl Compounds Catalyzed by Sn-Mont[a]

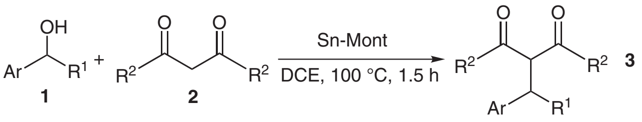


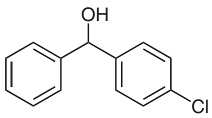
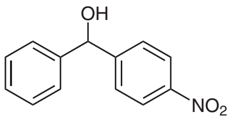
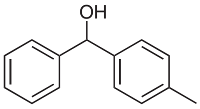
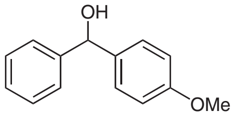
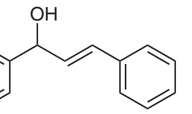
Entry	1,3-Dicarbonyl compound **2**		Time (h)	Product **3**	Yield (%)[b]
1	**2a**	$R^1 = R^2 = OMe$	1.5	**3aa**	90
2	**2b**	$R^1 = R^2 = OEt$	1.5	**3ab**	93
3	**2c**	$R^1 = R^2 = Me$	1	**3ac**	93
4	**2d**	$R^1 = Me, R^2 = Ph$	1	**3ad**	91
5	**2e**	$R^1 = R^2 = Ph$	1	**3ae**	98
6	**2f**	$R^1 = Me, R^2 = OEt$	1	**3af**	92

[a] Reaction conditions: Sn-Mont (25 mg, 4.75 mol%), **1a** (1 mmol), 1,3-dicarbonyl compounds **2** (1.5 mmol), DCE (2 mL), 100 °C.
[b] Isolated yields.

Various benzhydrol derivatives (**1b**–**e**) with different substituents on the benzene ring other than **1a** were also tested for the substitution reactions with a 1,3-diester **2a** or **2b** under the optimal conditions. The excellent yields (83–95%) of the alkylated diesters **3** were obtained regardless of having an electron-withdrawing or electron-donating group in **1** (Table 3, entries 1–7). Allylic alcohol **1f** also reacted with **2a** to give **3fa** in a moderate yield of 66% (entry 8).

Table 3 Reactions of Alcohols with 1,3-Diesters Catalyzed by Sn-Mont[a]



Entry	Alcohol **1**		Diester **2**	Product **3**	Yield (%)[b]
1	**1b**		**2a**	**3ba**	89
2	**1c**		**2a**	**3ca**	83
3	**1d**		**2a**	**3da**	93
4	**1e**		**2a**	**3ea**	90
5	**1b**		**2b**	**3bb**	85
6	**1d**		**2b**	**3db**	91
7	**1e**		**2b**	**3eb**	82
8	**1f**		**2a**	**3fa**	66

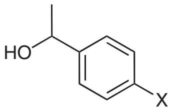
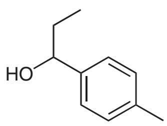
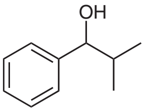
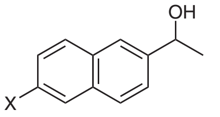
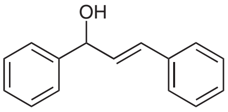
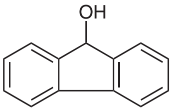
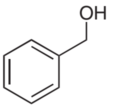
[a] Reaction conditions: Sn-Mont (25 mg, 4.75 mol%), **1** (1 mmol), 1,3-diesters **2** (1.5 mmol), DCE (2 mL), 100 °C, 1.5 h.
[b] Isolated yields.

To unveil the generality of the Sn-Mont-catalyzed reactions, the reactions of a more active acetylacetone (**2c**) with alcohols were examined (Table 4). α-Aryl alkanols and their derivatives with an electron-donating or electron-withdrawing group afforded the corresponding products **3** in good to excellent yields in 1–1.5 hours (entries 1–7). Allylic alcohol **1f** as well as α-diaryl methanols (**1a**, **1b**, **1d**, **1e**) gave good yields (entries 8–12). To our delight, a more sterically congested alcohol, 9-fluorenol (**1n**) was also applicable to afford **3nc** with a moderate yield of 70% in a little prolonged reaction time (3 h; entries 13), and the product was confirmed as a mixture of keto and enol forms by NMR.[32] Moreover, the reaction of a primary alcohol, benzyl alcohol (**1o**) with **2c** smoothly proceeded in 65% yield (entry 14). In all cases, the selective monoalkylation took place without dialkylation. Thus, it is concluded that the Sn-Mont catalytic system has the unique high activity for the nucleophilic substitution of α-aryl alcohols with a wide range of 1,3-dicarbonyl compounds, as summarized in Tables 2– 4.

Sn-Mont has Brønsted acidity confirmed by the FT-IR spectrum of Sn-Mont after pyridine adsorption.[25,28] Thus, the reaction pathway in the nucleophilic substitution of al-

Table 4 Reactions of Alcohols with Acetylacetone (**2c**) Catalyzed by Sn-Mont[a]

$$\mathbf{1} + \mathbf{2c} \xrightarrow[\text{DCE, 100 °C, 1–1.5 h}]{\text{Sn-Mont}} \mathbf{3}$$

Entry	Alcohol **1**		X	Product **3**	Yield (%)[b]
1	**1g**		H	**3gc**	93
2	**1h**		OMe	**3hc**	91
3	**1i**		Cl	**3ic**	82
4	**1j**			**3jc**	92
5	**1k**			**3kc**	79
6	**1l**		H	**3lc**	77
7	**1m**		OMe	**3mc**	80
8	**1f**			**3fc**	88
9	**1a**			**3ac**	93
10	**1b**			**3bc**	92
11	**1d**			**3dc**	86
12	**1e**			**3ec**	85
13[c]	**1n**			**3nc**	70[d]
14	**1o**			**3oc**	65[e]

[a] Reaction conditions: Sn-Mont (25 mg, 4.75 mol%), **1** (1 mmol), **2c** (1.5 mmol), DCE (2 mL), 100 °C, 1–1.5 h.

[b] Isolated yields.

[c] Sn-Mont (20 mg), **1m** (0.5 mmol), 3 h.

[d] Product **3nc** existed as a mixture of keto and enol forms.

[e] Determined by GC.

cohols with 1,3-dicarbonyl compounds should involve a carbocation intermediate derived from the dehydration of the protonated alcohol with the aid of Sn-Mont,[20] followed by the direct attack with 1,3-dicarbonyl compounds to form the alkylated 1,3-dicarbonyl derivatives.

In conclusion, we have developed an efficient and environmentally-friendly protocol for the direct nucleophilic substitution of benzylic alcohols with various 1,3-dicarbonyl compounds including 1,3-diesters in 1,2-dichloroethane using a catalytic amount of a solid Brønsted catalyst, Sn-Mont. The reactions smoothly proceeded even in the crude solvent without any formation of waste salts. In all cases, the desired alkylated products were obtained in moderate to excellent yields in short reaction times. Therefore, easily prepared, water-tolerant, reusable, highly active, and nontoxic Sn-Mont has great potential in organic synthesis by replacing the previously-reported homogeneous catalysts, most of which are hydrolyzable, expensive, or toxic.

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References and Notes

(1) Yasuda, M.; Somyo, T.; Baba, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 793.

(2) Bandini, M.; Eichholzer, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9608.

(3) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 2605.

(4) Rueping, M.; Nachtsheim, B. J.; Kuenkel, A. *Org. Lett.* **2007**, *9*, 825.

(5) Kischel, J.; Mertins, K.; Michalik, D.; Zapf, A.; Beller, M. *Adv. Synth. Catal.* **2007**, *349*, 865.

(6) Kothandaraman, P.; Rao, W. D.; Zhang, X. X.; Chan, P. W. H. *Tetrahedron* **2009**, *65*, 1833.

(7) (a) Cella, J. A. *J. Org. Chem.* **1982**, *47*, 2125. (b) Schmitt, A.; Reissig, H. U. *Eur. J. Org. Chem.* **2000**, 3893. (c) Rubin, M.; Gevorgyan, V. *Org. Lett.* **2001**, *3*, 2705. (d) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 1414. (e) Nishimoto, Y.; Kajioka, M.; Saito, T.; Yasuda, M.; Baba, A. *Chem. Commun.* **2008**, 6396.

(8) Wang, J. C.; Masui, Y.; Onaka, M. *Tetrahedron Lett.* **2010**, *51*, 3300.

(9) Qin, H. B.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 409.

(10) (a) Noji, M.; Ohno, T.; Fuji, K.; Futaba, N.; Tajima, H.; Ishii, K. *J. Org. Chem.* **2003**, *68*, 9340. (b) Jana, U.; Maiti, S.; Biswas, S. *Tetrahedron Lett.* **2008**, *49*, 858. (c) Ohshima, T.; Miyamoto, Y.; Ipposhi, J.; Nakahara, Y.; Utsunomiya, M.; Mashima, K. *J. Am. Chem. Soc.* **2009**, *131*, 14317. (d) Shi, F.; Tse, M. K.; Cui, X. J.; Gordes, D.; Michalik, D.; Thurow, K.; Deng, Y. Q.; Beller, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 5912.

(11) (a) Chen, G.; Wang, Z.; Wu, J.; Ding, K. L. *Org. Lett.* **2008**, *10*, 4573. (b) Rajagopal, G.; Kim, S. S. *Tetrahedron* **2009**, *65*, 4351.

(12) Vicennati, P.; Cozzi, P. G. *Eur. J. Org. Chem.* **2007**, 2248.

(13) Sanz, R.; Martinez, A.; Miguel, D.; Alvarez-Gutierrez, J. M.; Rodriguez, F. *Adv. Synth. Catal.* **2006**, *348*, 1841.

(14) (a) Noji, M.; Konno, Y.; Ishii, K. *J. Org. Chem.* **2007**, *72*, 5161. (b) Babu, S. A.; Yasuda, M.; Tsukahara, Y.; Yamauchi, T.; Wada, Y.; Baba, A. *Synthesis* **2008**, 1717. (c) Wu, J.; Ye, J. H.; Hu, J. S.; Wang, Z. Y.; Shang, Y. J. *Chin. J. Org. Chem.* **2009**, *29*, 462. (d) Thirupathi, P.; Kim, S. S. *Tetrahedron* **2010**, *66*, 2995.

(15) Yuan, Y.; Shi, Z. Z.; Feng, X.; Liu, X. N. *Appl. Organomet. Chem.* **2007**, *21*, 958.

(16) Shushizadeh, M. R.; Kiany, M. *Chin. Chem. Lett.* **2009**, *20*, 1068.

(17) Sanz, R.; Miguel, D.; Martinez, A.; Alvarez-Gutierrez, J. M.; Rodriguez, F. *Org. Lett.* **2007**, *9*, 2027.

(18) Funabiki, K.; Komeda, T.; Kubota, Y.; Matsui, M. *Tetrahedron* **2009**, *65*, 7457.

(19) (a) Yadav, J. S.; Reddy, B. V. S.; Pandurangam, T.; Rao, K. V. R.; Praneeth, K.; Kumar, G.; Madavi, C.; Kunwar, A. C. *Tetrahedron Lett.* **2008**, *49*, 4296. (b) Wang, G. W.; Shen, Y. B.; Wu, X. L. *Eur. J. Org. Chem.* **2008**, 4999.

(20) Motokura, K.; Nakagiri, N.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2007**, *72*, 6006.

(21) (a) Pinnavaia, T. J. *Science* **1983**, *220*, 365. (b) Laszlo, P. *Science* **1987**, *235*, 1473. (c) Izumi, Y.; Onaka, M. *Adv. Catal.* **1992**, *38*, 245.

(22) (a) Onaka, M.; Ohno, R.; Kawai, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2689. (b) Kawai, M.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2157. (c) Kawai, M.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1237. (d) Higuchi, K.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2016. (e) Onaka, M.; Higuchi, K.; Nanami, H.; Izumi, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2638.

(23) Onaka, M.; Hosokawa, Y.; Higuchi, K.; Izumi, Y. *Tetrahedron Lett.* **1993**, *34*, 1171.

(24) Wang, J. C.; Masui, Y.; Watanabe, K.; Onaka, M. *Adv. Synth. Catal.* **2009**, *351*, 553.

(25) Masui, Y.; Wang, J. C.; Onaka, M. *to be submitted.*

(26) Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Eur. J.* **2005**, *11*, 288.

(27) (a) Ebitani, K.; Ide, M.; Mitsudome, T.; Mizugaki, T.; Kaneda, K. *Chem. Commun.* **2002**, 690. (b) Ebitani, K.; Kawabata, T.; Nagashima, K.; Mizugaki, T.; Kaneda, K. *Green Chem.* **2000**, *2*, 157. (c) Kaneda, K. *Synlett* **2007**, 999.

(28) Wang, J. C.; Masui, Y.; Onaka, M. *Eur. J. Org. Chem.* **2010**, 1763.

(29) **General Procedure for Sn-Mont-Catalyzed Nucleophilic Substitution of Alcohols with 1,3-Dicarbonyl Compounds**: In a flask were placed Sn-Mont (25 mg, 4.75 mol%) which was activated at 120 °C for 1 h in a vacuum, 1,2-dichloroethane (2 mL), which was not required to be dehydrated, benzhydrol (**1a**; 1 mmol), and dimethyl malonate (**2a**; 1.5 mmol). The resultant mixture was stirred vigorously at 100 °C under reflux. After the completion of the reaction monitored with TLC, the catalyst was removed by filtration through a Celite plug, followed by being washed with CH_2Cl_2. The combined solution was evaporated under reduced pressure to give the crude product. Further purification was carried out by silica gel chromatography (eluting solvent: hexane–EtOAc, 8:1) to give the desired **3aa** as a white solid in 90% yield.

(30) (a) Kugita, T.; Jana, S. K.; Owada, T.; Hashimoto, N.; Onaka, M.; Namba, S. *Appl. Catal. A: Gen.* **2003**, *245*, 353. (b) Wang, J.; Liu, Q. F.; Liu, Q. *Microporous Mesoporous Mat.* **2007**, *102*, 51. (c) Wang, J.; Liu, Q. *Solid State Commun.* **2008**, *148*, 529.

(31) Spectroscopic data for selected products: 3-(Diphenylmethyl)-pentane-2,4-dione (**3aa**): white solid; mp 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.00$ (s, 6 H), 4.73 (d, $J = 12.3$ Hz, 1 H), 4.81 (d, $J = 12.3$ Hz, 1 H), 7.10–7.20 (m, 2 H), 7.25–7.30 (m, 8 H). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 29.7$, 51.2, 74.5, 127.0, 127.7, 128.9, 141.2, 203.0. HRMS: *m/z* calcd for $C_{18}H_{18}O_2$: 266.1307; found: 266.1312. Dimethyl 2-(Diphenylmethyl)malonate (**3ac**): white solid; mp 88–90 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.54$ (s, 6 H), 4.36 (d, $J = 12.3$ Hz, 1 H), 4.77 (d, $J = 12.3$ Hz, 1 H), 7.15–7.20 (m, 2 H), 7.24–7.30 (m, 8 H). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 51.1$, 52.6, 57.2, 126.9, 127.7, 128.6, 141.1, 168.0. HRMS: *m/z* calcd for $C_{18}H_{18}O_4$: 298.1205; found: 298.1199. Ethyl 3-Oxo-2-(diphenylmethyl)butanoate (**3af**): white solid; mp 87–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.00$ (t, $J = 7.1$ Hz, 3 H), 2.09 (s, 3 H), 4.00 (q, $J = 7.1$ Hz, 2 H), 4.53 (d, $J = 12.3$ Hz, 1 H), 4.76 (d, $J = 12.3$ Hz, 1 H), 7.15–7.25 (m, 2 H), 7.24–7.35 (m, 8 H). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta =$ 13.7, 30.0, 50.9, 61.5, 65.2, 126.8, 126.9, 127.7, 127.8, 128.6, 128.8, 141.2, 141.5, 167.6, 201.8. HRMS: *m/z* calcd for $C_{19}H_{20}O_3$: 296.1412; found: 296.1423.

(32) Morenomanas, M.; Gonzalez, A.; Marquet, J.; Sanchezferrando, F. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1827.