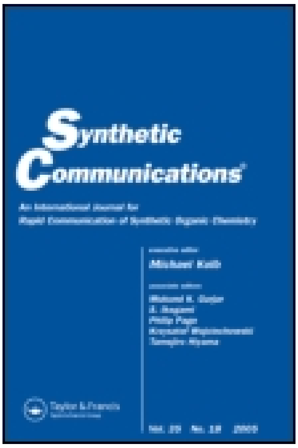

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$HClO_4$-SiO_2 as an Efficient and Recyclable Catalyst for the Synthesis of Amide Derivatives

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$HClO_4$-SiO_2 AS AN EFFICIENT AND RECYCLABLE CATALYST FOR THE SYNTHESIS OF AMIDE DERIVATIVES

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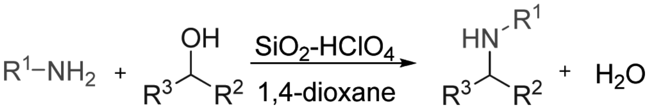
GRAPHICAL ABSTRACT



Abstract *An efficient and clean procedure for amide alkylation is reported by direct condensation of equimolar amounts of benzylic and allylic alcohols with primary amides in the presence of silica perchloric acid ($HClO_4$-SiO_2). The direct condensation of secondary benzylic and allylic alcohols with benzamide, sulfonamide, 2-furamide, cinnamamide, and acrylamide has been achieved to afford the corresponding amide in excellent yields. The convenient, recyclable, and excellent yields of products are attractive features of this reaction.*

Keywords Amide alkylation reactions; heterogeneous; recyclable; silica perchloric acid ($HClO_4$-SiO_2)

INTRODUCTION

C–N bond formation is an important reaction in organic synthesis because of the importance of nitrogen-containing compounds in the production of pharmaceuticals and fine chemicals.[1] Traditionally, substitution reactions of alkyl halides, alkyl acetates, or related compounds with amine nucleophiles are one of the most useful types of C–N bond-forming reactions.[2] In contrast to traditional methods, a good alternative approach is the nucleophilic substitution of the hydroxy groups in alcohols with various amines, which is one of the most efficient and reliable methods.[3] However, these methods produce stoichiometric amounts of salt waste both in preactivation of the alcohols and the C–N bond-formation steps. Hence,

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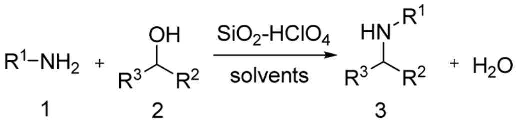
in view of the demand for more atom-economical, ecofriendly, and convenient processes, the direct catalytic substitution of alcohols with amines is desirable.

Over the years, a number of amide alkylation reactions by direct substitution of alcohols with amines in the presence of transition metals with ligands, such as Pd and Ru, have been reported.[4] However, the use of weak nitrogen nucleophiles such as amides which are easily available, are extremely rare and require high temperatures. Very recently, more and more groups have turned their attentions to Lewis acid–catalyzed amidation reactions of alcohols with primary amides. A series of Lewis acid such as $NaAuCl_4$,[5a] $MoCl_5$,[5b] H-montmorillonite,[5c] $FeCl_3$,[5d] 12-phosphotungstic acid (PWA),[5e] a combination of $Bi(OTf)_3$,[5f] with KPF_6 as additive, and water-soluble calix[4]resorcinarene sulfonic acid have been reported.[5g] While these methodologies involved mild conditions and display increased functional group tolerance, most of them suffer from unsatisfactory yields, expensive require and detrimental metal precursors, and are also difficult to recycle, which limits their use. Therefore, development of a more practical and atom-economical method for direct substitution of primary amides with benzylic or allylic alcohols has acquired relevance to current research.

Recently, $HClO_4$-SiO_2 has gained more and more attention because of its outstanding qualities; new, heterogeneous, highly efficient, inexpensive, reusable, and it is environmentally friendly. It has been utilized successfully in several organic transformations to minimize undesirable waste causing environmental pollution, including acylationreactions,[6a–6c] selective removal of anomeric *o*-acetate groups in carbohydrates,[6d] the Ferrier rearrangement,[6e] the Hantzsch and Knoevenagel condensations,[6f] the aza-Michael addition of amines to activated alkenes,[6g] electrophilic substitution reaction,[6h] and synthesis of privileged heterocyclic compounds through multicomponent reactions.[6i,6g] It is well known that perchlorates can give rise to explosive reactions when heated at high temperatures in the presence of combustible compounds.[7a] Therefore, the potential hazard connected with their manufacture and use has prevented their extensive application in industrial processes,[6a] especially when large amounts of these compounds are involved. However, recent reported methods indicate that low catalyst loading of $HClO_4$-SiO_2 can effectively bring about the organic transformations and can be operated even at 90 °C.[7b] In this article, we report $HClO_4$-SiO_2 as an efficient catalyst for the synthesis of amide derivatives by direct substitution of benzylic and allylic alcohols with various carboxamides or sulfonamides (Scheme 1).



R^1 = PhCO, Ts or CH_2=CHCO
R^2 = alkyl, aryl or allyl
R^3 = alkyl, aryl or allyl

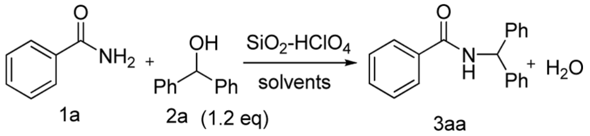
Scheme 1. $HClO_4$-SiO_2-catalyzed amidation of benzylic/allylic alcohols.

RESULTS AND DISCUSSION

Our initial efforts were directed to the optimization of the reaction conditions, which were examined in the reaction between benzyl amide **1a** and diphenyl methanol **2a** in the presence of 5 mol% $HClO_4$-SiO_2 under reflux condition (Table 1). Initially, we tested a series of solvents, such as H_2O, CH_3CN, tetrahydrohuran (THF), CH_2Cl_2, and 1,4-dioxane. It was found that the reaction took place in CH_3CN, giving the desired product in 72% yield (entry 2), while no products were detected in H_2O even after 6 h (entry 1). Besides, the reactions that occurred in CH_2Cl_2 and THF did not furnish satisfactory results after 4 h (entries 3 and 4). To our satisfaction, when this reaction was performed in 1,4-dioxane, the product was obtained in excellent yield of 93% after only 3 h (entry 5). Therefore, 1,4-dioxane was chosen as a solvent for further reaction optimization with respect to reaction time and the maximum yield of the products. In the study of catalyst loading, 0%, 2%, and 10 mol% of $HClO_4$-SiO_2 were tested. No product was obtained after 6 h in the presence of silica gel alone (entry 6); the reaction with 10 mol% catalyst gave 95% yield (entry 8) in 3 h, whereas 2 mol% catalyst loading only gave 77% yield (entry 7). These results suggested that the optimal amount of $HClO_4$-SiO_2 was 5 mol%, and that greater amounts of the catalyst did not increase the yield noticeably.

Because reducing the amount of catalyst and making it reusable are two important aspects of green chemistry, we tested the activity of the recovered catalyst $HClO_4$-SiO_2. After each reaction, the reaction mixture was filtered. The catalyst was washed with $CHCl_3$ (2 × 5 mL), EtOH (2 × 5 mL), and Et_2O (2 × 5 mL) and subsequently dried at 80 °C for reuse directly in the next cycle. Activity of catalyst was retained after being recycled multiple times. Even after recycling the catalyst four times, the yields were practically identical to those observed when fresh catalyst was used (Table 1, entry 5).

Table 1. Solvent effect on the synthesis catalyzed by $HClO_4$-SiO_2[a]



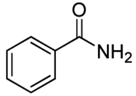
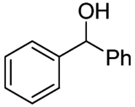
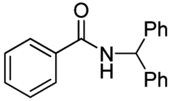
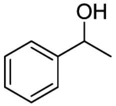
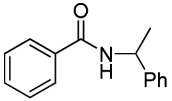
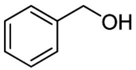
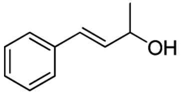
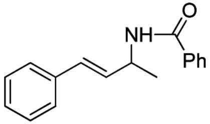
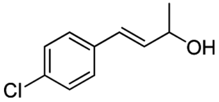
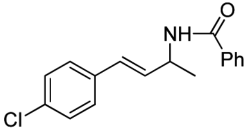
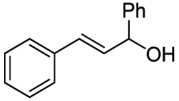
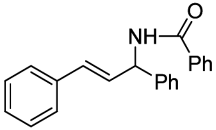
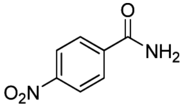
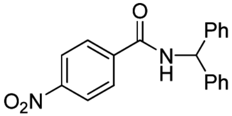
Entry	Solvent	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	H_2O	5	6	—
2	CH_3CN	5	4	72
3	THF	5	4	16
4	CH_2Cl_2	5	4	Trace
5[c]	1,4-Dioxane	5	3	93, 91, 88, 92, 91
6	1,4-Dioxane	0	6	—
7	1,4-Dioxane	2	3	77
8	1,4-Dioxane	10	3	95

[a] Unless otherwise specified, all reactions were performed with **1a** (1 mmol), **2a** (1 mmol), and $HClO_4$-SiO_2 in solvent (2 mL) under reflux conditions.

[b] Isolated yield.

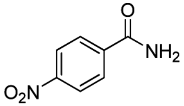
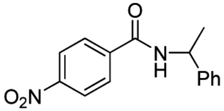
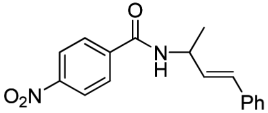
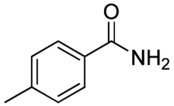
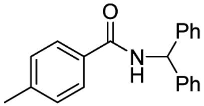
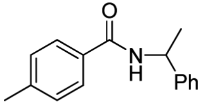
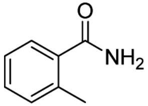
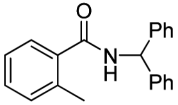
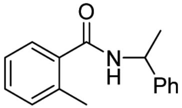
[c] The yields corresponded to the recycling reusability of catalyst.

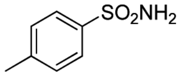
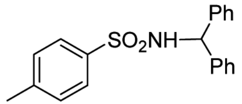
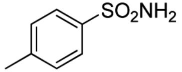
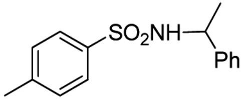
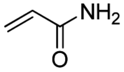
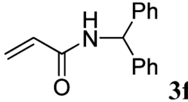
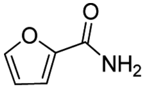
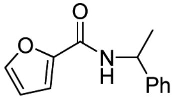
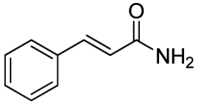
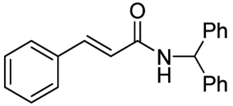
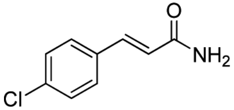
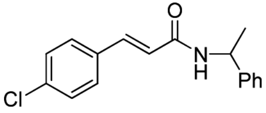
Table 2. $HClO_4$-SiO_2-catalyzed substitution of various alcohols **2** with amides[a]

Entry	Nucleophile	Alcohol	Product	Time (h)	Yield[b] (%)
1	 **1a**	 **2a**	 **3aa**	3	93
2	**1a**	 **2b**	 **3ab**	3	83
3	**1a**	 **2c**	—	4	—
4	**1a**	 **2d**	 **3ad**	3	60
5	**1a**	 **2e**	 **3ae**	3	56
6	**1a**	 **2f**	 **3af**	3	86
7	 **1b**	**2a**	 **3ba**	3	88

(*Continued*)

Table 2. Continued

Entry	Nucleophile	Alcohol	Product	Time (h)	Yield^{b} (%)
8	 **1b**	**2b**	 **3bb**	4	78
9	**1b**	**2d**	 **3bd**	4	67
10	 **1c**	**2a**	 **3ca**	3	95
11	**1c**	**2b**	 **3cb**	4	84
12	 **1d**	**2a**	 **3da**	5	82
13	**1d**	**2b**	 **3db**	5	63

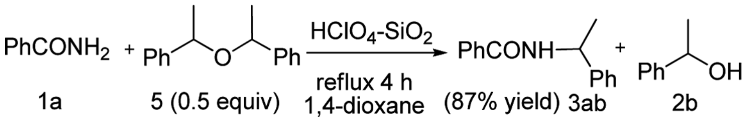
14	 **1e**	**2a**	 **3ea**	3	96
15	 **1e**	**2b**	 **3eb**	3	85
16	 **1f**	**2a**	 **3fa**	3	85
17	 **1g**	**2b**	 **3gb**	4	68
18	 **1h**	**2a**	 **3ha**	3	87
19	 **1i**	**2b**	 **3ib**	4	72
20	$CH_3CONH_2^{1j}$ **1j**	**2a**	/	4	/

[a] Reaction condition: nucleophile 1 (1 mmol), alcohol 2 (1 mmol), $HClO_4$-SiO_2 (0.05 mmol), 1,4-dioxane (2 mL).
[b] The yield refers to pure isolated product characterized from spectral data.

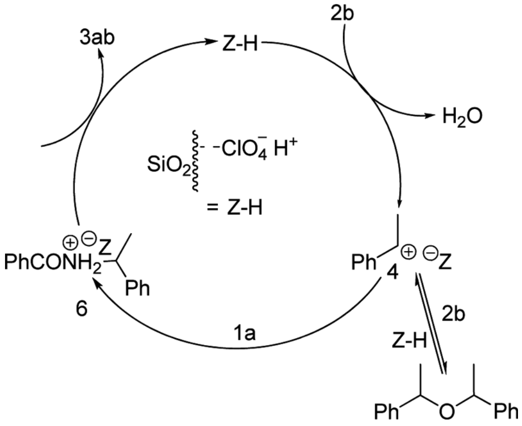
Encouraged by the results obtained for benzyl amide **1a** and diphenyl methanol **2a**, we investigated a number of alcohol substrates and various types of nitrogen nucleophiles to probe their behaviors under the current catalytic conditions (Table 2). In general, the reactions proceeded efficiently with various substituted secondary benzyl alcohols and unsaturated primary amides in excellent yields within short period of time. Obviously, secondary benzylic alcohols afforded the corresponding product with greater yields than secondary allylic alcohols (entries 1, 2, and 4–6), but no corresponding products were detected when using benzyl alcohol under these conditions, even after prolonged heating (entry 3). The present method was equally effective for benzyl amide with electron-donating groups such as *p*-methyl-benzamide (entries 10 and 11), which gaves lightly greater yields (84–95%) than electron-donating groups of *p*-nitro-benzamide (78–88%) (entries 7 and 8). In contrast, *p*-methyl-benzamide favored the formation of product with greater yield and needed less time than *o*-methyl-benzamide (entries 12 and 13); the steric effects of *o*-methyl should be responsible for this. Furthermore, this reaction was also applied to *p*-toluenesulfonamide **1e**, acrylamide **1f,** 2-furamide **1g**, cinnamamide **1h**, and 4-chloro cinnamamide **1i**. All of them underwent smooth amidation with diphenyl methanol **2a** or 1-phenylethanol **2b** and gave the desired products in yields of 68–96% (entries 14–19). Although this reaction was highly efficient for these types of amides, acetamide **1j** itself did not react under these conditions even with prolonged heating (entry 20).

Although many people have probed the Lewis acid-catalyzed reaction mechanism of the amide alkylation reactions, the exact reaction mechanism is not quite clear at the moment. For example, Wang et al. have recently reported that (*R*)-1-phenylethanol [99% *ee*] and *p*-toluenesulfonamide were activated by the Lewis acid to produce the final product in excellent yield as a racemic mixture and proposed the S_N1 mechanism for the reaction.[5e] Jana et al. have reported that the benzylic alcohols were first converted to the corresponding dimeric ether and then activated by the Lewis acid to produce the final product by nucleophilic substitution with the amide,[5d] but this mechanism has not been proved by corresponding experiment.

To further verify the Lewis acid–catalyzed amide alkylation reaction mechanism, we designed the following experiment (Scheme 2). First, 1-phenylethanol **2b** was converted to the corresponding dimeric ether **5** (0.5 equiv) and then treated with benzyl amide **1a** and $HClO_4$-SiO_2 under the typical reaction conditions. After 3h, the final product **3ab** was isolated in 87% yield, which was almost equal to the previous yield of 83% (entry 1). In light of these results, we think that the reaction proceeds through the catalytic cycle described in Scheme 3. The reaction occurs in the catalyst surface,[8] in which the interaction between **2b** and Z-H ($HClO_4$-SiO_2) generates the intermediate **4**. This, reacting with **1a**, gives rise to the key intermediate



Scheme 2. Amide alkylation reactions of **la** with **2b**.



Scheme 3. Catalytic cycle mechanism.

6, which releases the product **3ab** with regeneration the catalyst of Z-H. Then, Z-H is ready to start another catalytic cycle. It is worthy of note that this process is the main mechanism of the amide alkylation reactions. Additionally, the intermediate **4** reacts with **2a** to furnish **5**, which could be regenerated as **4** in the presence of $HClO_4$-SiO_2 to participate in the next cycle of reaction.

CONCLUSIONS

In summary, we have developed a novel and facile method for the synthesis of amide derivatives in the presence of solid-supported $HClO_4$-SiO_2 as a heterogeneous catalyst. The present methodology offers very attractive features such as ease of recovery, reuse of the catalyst, benign reaction, excellent yields, and a waste-free chemical process.

EXPERIMENTAL

Characterization of all compounds was done with ^1H NMR and mass spectrometry. ^1H NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz). Electrospray ionization (ESI) mass spectra were obtained on a Mariner System 5303 mass spectrometer. Melting points were measured with an SGWX-4 apparatus and are uncorrected.

Preparation of the Catalyst

$HClO_4$ (1.25 g, 12.5 mmol, as a 70% aqueous solution) was added to the suspension of silica gel (23.75 g, 230–400 mesh) in diethyl ether (75 mL). The mixture was concentrated, and the residue was dried under vaccum at 100 °C for 72 h to afford $HClO_4$–SiO_2 (0.5 mmol g^{-1}) as a free-flowing powder.[7c]

General Procedure for the Preparation of 3aa

To a stirred solution of benzamide **1a** (128 mg, 1 mmol) and diphenyl methanol **2a** (220 mg, 1.2 mmol) in dry 1,4-dioxane (2 mL) was added $HClO_4$–SiO_2 (100 mg, 0.05 mmol). The resulting reaction mixture was refluxed for 3h. The reaction mixture was then concentrated under reduced pressure and loaded onto a silica-gel column and chromatographed with petroleum etherl/ethyl acetate (4:1) to obtain a white solid (93%).

Selected Spectroscopic Data

N-(1-Phenylethyl)benzamide (3ab). White solid, mp 120–122 °C. ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 1.62 (d, $J = 6.9$ Hz, 3H), 5.34 (m, 1H), 6.28 (d, $J = 3.8$ Hz, 1H), 7.29 (m, 2 H), 7.34–7.46 (m, 6 H), 7.48–7.51 (m, 2H), 7.78 (d, $J = 7.3$ Hz, 2H). ESI-MS: m/z 225.1 $[M+H]^+$.

N-(Diphenylmethyl)-4-nitro-benzamide (3ba). White solid, mp 216–218 °C. ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 6.47 (d, $J = 8.0$ Hz, 1 H), 7.28–7.38 (m, 1H), 8.23–8.30 (m, 4H), 9.72 (d, $J = 8.0$ Hz, 1H). ESI-MS: m/z 332.1 $[M+H]^+$.

N-(4-Methylbenzoyl)-α-methylbenzylamine (3cb). White solid, mp 127–128 °C. ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 1.58 (d, $J = 6.9$ Hz, 3H), 2.36 (s, 1H), 5.28–5.47 (m, 1H), 6.40 (br s, 1H), 7.12–7.16 (d, $J = 7.8$ Hz, 2H), 7.32–7.43 (m, 5 H), 7.67 (d, $J = 7.8$ Hz, 2H). ESI-MS: m/z 239.0 $[M+H]^+$.

N-(Diphenylmethyl-)-2-toluamide (3da). White solid, mp 159–160 °C. ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 2.48 (s, 3H), 6.48 (br d, 1H), 6.43 (br d, 1H, $J = 7.8$ Hz), 6.62–6.76 (m, 1H), 7.23–7.42 (m, 10H), 7.60–7.67 (m, 4H). ESI-MS: m/z 301.2 $[M+H]^+$.

N-Benzhydryl-4-toluenesulfonamide (3ea). White solid, mp 155–156 °C. ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 2.38 (s, 3H), 5.02 (d, 1H, $J = 6.6$ Hz), 5.57 (d, 1H, $J = 6.9$ Hz), 7.08–7.11 (m, 4H), 7.12–7.16 (d, 2H, $J = 6.9$ Hz), 7.18–7.12 (m, 6H), 7.53–7.58 (d, 2H, $J = 8.0$ Hz). ESI-MS: m/z 337.1 $[M+H]^+$.

N-(1-Phenylethyl)-4-methylbenzenesulfonamide (3eb). White solid, mp 78–79 °C. ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 1.51 (d, 3 H, $J = 6.8$ Hz), 2.37 (s, 3H), 4.45 (m, 1H), 4.92 (d, 1H, $J = 6.8$ Hz), 7.08–7.11 (m, 2H), 7.17–7.22 (m, 5H), 7.62 (d, 2H, $J = 8.2$ Hz). ESI-MS: m/z 275.1 $[M+H]^+$.

N-(Diphenylmethyl)propenamide (3fa). White solid, mp 177–179 °C. ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 5.69 (d, 1 H, $J = 10.2$ Hz), 6.14 (br s, 1H), 6.16–6.20 (dd, 2H, $J = 17.0$, 10.2 Hz), 6.33 (s, 1H), 6.36 (d, 2H, $J = 17.0$ Hz), 7.25–7.29 (m, 6H), 7.32–7.35 (m, 4H). ESI-MS: m/z 237.2 $[M+H]^+$.

N-(1-Methylbenzyl)-3-(p-chlorophenyl)propenamide (3ib). White solid, mp 142–144 °C; ^1H NMR ($CDCl_3$, 500 Hz) δ_H (ppm): 1.50 (d, $J = 7.0$ Hz, 3H), 4.90–5.04 (dd, $J = 7.0$ Hz, 1H), 6.11 (br s, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 7.27–7.47 (m, 9H), 7.62 (d, $J = 16.0$ Hz, 1H). ESI-MS: m/z 285.1 $[M+H]^+$.

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