Bismuth sulfonate immobilized on silica gel for allylation of aldehydes and synthesis of homoallylic amines

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Catalytic allylation of aldehydes and the synthesis of homoallylic amines using bismuth sulfonate immobilized on silica gel in presence of allyltributylstannane are reported for the first time. The reaction proceeds smoothly with the aid of benzoic acid as an additive and provides corresponding homoallylic alcohols and homoallylic amines in good yields. The catalyst can be reused five times without significant loss of the catalytic activity.

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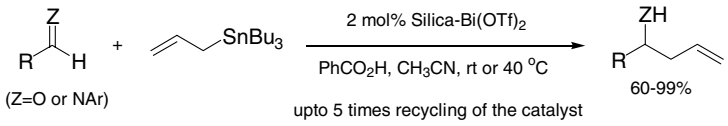

KEY WORDS: allylations; heterogeneous catalysis; silica gel; bismuth sulfonate; recycling.

1. Introduction

Lewis acid (LA)-catalyzed carbon–carbon bond forming reactions are of great importance in organic synthesis due to their high selectivity and reactivity under mild reaction conditions [1–3]. Among them, LA-catalyzed allylation of aldehydes [4–6] and aldimines [7–9] has become useful carbon–carbon bond forming reactions in generating homoallylic alcohols and amines, respectively. Generally, the preparation of homoallylic alcohols and amines is accomplished either by nucleophilic addition of organometallic reagents or by addition of allylsilane, allyltin, allylborane or allylgermane reagents in the presence of LA catalysts [6]. Various LA catalysts such as $TiCl_4$ or $BF_3.OEt_2$ [7–9], transition metal reagents such as $PdCl_2(PPh_3)_2$ or $PtCl_2(PPh_3)_2$ [10], lanthanide triflates [11–12] and others [13–14] have been employed for the transformations. However, these reagents are often associated with problems such as high cost, sensitivity towards air and moisture, and difficulty in handling especially on a large scale. To circumvent some of these problems, recently many new methods have been developed for the transformations [15–20]. In this regard, lanthanide triflates in combination with rate accelerating reagents such as benzoic acid [16] or sodium dodecyl sulfate (SDS) [17] as catalysts for allylation of aldehydes and aldimines have received keen attention from organic chemists. Desirable yet are more efficient and economic LA catalysts for allylation reactions and recycling of catalysts using heterogeneous support materials can be an attractive alternative. Toward this direction, a recent procedure employing bismuth triflate [20] attracted our attention.

Homogeneous catalysts provide good selectivity and reactivity, however, often the high price and sensitivity towards environment of the catalysts prohibit them from being used in practical applications. Heterogenization of homogeneous catalysts can render the reaction process convenient and economic. Recently we have reported a lanthanum catalyst grafted onto mesoporous silica support for allylation in aqueous medium [21]. Herein we describe a simple and efficient protocol for allylation of aldehydes and *in situ* generated aldimines for the first time using bismuth sulfonate immobilized on silica [Si–$Bi(OTf)_2$] as a catalyst.

2. Experimental

2.1. Preparation of catalyst

Silica gel (1.00 g) was heated with 3-(mercapto)propyltrimethoxysilane (5.0 mL) in dry toluene (10 mL) for 24 h at reflux. The material was filtered and extracted for 12 h with CH_2Cl_2/Et_2O (1:1 v/v) mixture, then dried *in vacuo*. The mercaptopropyl-grafted silica was oxidized with H_2O_2 (excess) in methanol (10 mL) for 24 h at room

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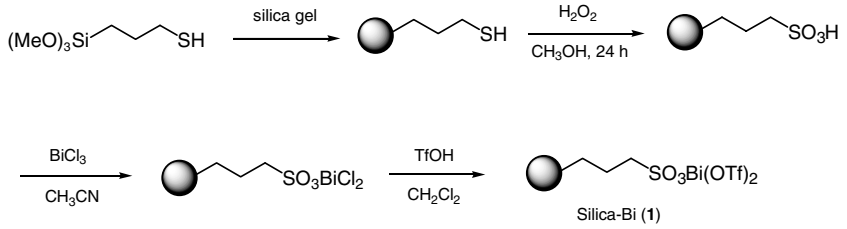


Scheme 1. Synthesis of bismuth sulfonate immobilized on silica.

temperature (RT). After sulfonation the material was treated with bismuth(III)chloride (1.5 mmol, 474 mg) in acetonitrile (10 mL) at reflux for 24 h. After cooling to RT, CH_3CN (10 mL) was added and the mixture was filtered, washed with CH_3CN (100 mL) and dried *in vacuo* to afford the silica supported bismuth chloride. Finally, this material was treated with trifluromethanesulfonic acid (187 mg, 1.24 mmol) in dichloromethane (10 mL) at RT for 12 h. Water (10 mL) was added and then the mixture was filtered and washed with H_2O, H_2O–THF, THF, Et_2O and dried *in vacuo* to afford **1** (see scheme 1).

2.2. Characterization

Samples of pure silica gel (200–400 mesh) and silica gel immobilized with $Bi(OTf)_3$ were subjected to TG-SDTA measurements. The decomposition behavior of free silica and Si–$Bi(OTf)_2$ has been compared to address the type and site of the linkage of the catalyst. Total loss of organic moiety as revealed in the thermogram from 240 to 880 °C accounts to 14.6%, which is approximately equivalent to the loss of organic moiety, i.e. 0.53 mmol/g present in Si–$Bi(OTf)_2$. From elemental analysis, it was found that the bismuth sulfonate immobilized on silica contained 4.8% of S, which corresponds to 1.5 mmol/g. ICP-MS verified the existence of bismuth metal (0.51 mmol/g) in the catalyst **1**.

3. Catalytic reactions

3.1. Typical experimental procedure for the allylation of aldehydes

To a stirred solution of *p*-chlorobenzaldehyde (0.40 mmol) in acetonitrile (3.0 mL), allyltributylstannane (0.40 mmol), benzoic acid (0.40 mmol) and Si–$Bi(OTf)_2$ (2.0 mol%) were added at RT and the mixture was stirred at RT. The progress of the reaction was monitored with TLC. After completion of the reaction, the catalyst was filtered and washed with acetonitrile. The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel (10% v/v ethyl acetate–hexane) to afford the desired adduct in 92% yield. The recovered catalyst was reused five times without loss of activity. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (d, 1H, OH), 2.52 (m, 2H, CH_2), 4.75 (t, 1H, CH), 5.2 (m, 2H, 2 vinyls), 5.82 (m, 1H, vinyl), 7.20–7.30 (m, 4H, aromatic).

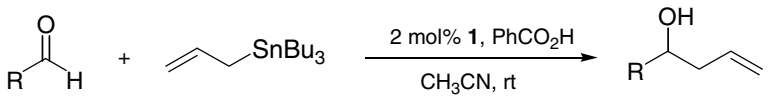
3.2. Typical experimental procedure for the allylation of in situ generated aldimines

To a stirred solution of *p*-chlorobenzaldehyde (0.40 mmol) in acetonitrile (3.0 mL) at 40 °C, allyltributylstannane (0.40 mmol), benzoic acid (0.40 mmol) and *o*-bromoaniline (0.40 mol), and Si–$Bi(OTf)_2$ (2.0 mol%) were added. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered and washed with acetonitrile (10 mL). The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel (10% v/v ethyl acetate–hexane) to afford the allylated product in 75% yield (entry 2, table 2). The recovered catalyst was reused five times without loss of catalytic activity. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52 (m, 2H, CH_2), 4.40 (t, 1H, CH), 5.2 (m, 2H, 2 vinyls), 5.82 (m, 1H, vinyl), 6.20 (d, 1H, aromatic), 6.60 (m, 2H, aromatic), 6.80–7.00 (m, 1H, aromatic), 7.20–7.30 (m, 4H, aromatic).

3.3. Results and discussion

We first studied the allylation of *p*-chlorobenzaldehyde with allyltributylstannane using 2.0 mol% of Si–$Bi(OTf)_2$ in acetonitrile at RT. The reaction was very slow and a 30% conversion was observed after 24 h. However, addition of one equivalent benzoic acid as an additive [16,20] accelerated the reaction providing the corresponding homoallylic alcohol in an excellent yield (92%). Encouraged by this result, we have carried out allylation of a variety of aldehydes to probe the scope and reactivity of the new catalyst system and the results are summarized in table 1. As can be seen from table 1, reactions with most of the aldehydes examined provided good to excellent yields of homoallylic alcohols with exception of 4-methoxybenzaldehde, where 62% yield of the desired product was obtained. It is of particular note that, in the case of *p*-nitrobenzaldehyde, 92% yield of the desired product was obtained even after 5th recycle of the catalyst (entry 2). When control reactions were carried out without the Bi catalyst under otherwise the same reaction conditions, no homoallylic alcohols were obtained at all either in the presence or absence of silica gel, suggesting the critical role of the bismuth catalyst.

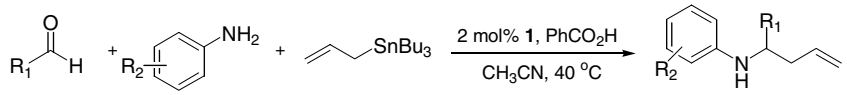
Table 1
Results of allylation reactions catalyzed by Si–Bi(OTf)$_2$



Entry	R	Time (min)	Yield (%)[a]
1	C_6H_5	40	80
2	4-NO_2–C_6H_5	30	99 (92)[b]
3	4-OMe–C_6H_5	60	62
4	4-Br–C_6H_5	45	85
5	4-Cl–C_6H_5	45	92
6	C_6H_5CH:CH	50	77
7	$CH_3(CH_2)_5$	40	80

[a]Yields of isolated products.
[b]yield after 5th recycle.

Table 2
Synthesis of homoallylamines catalyzed by Si–Bi(OTf)$_2$ at 40 °C



Entry	R_1	R_2	Time (min)	Yield (%)[a]
1	Ph	*o*-Br	45	80
2	*p*-Cl–Ph	*o*-Br	40	75 (70)[b]
3	*p*-Br–Ph	*o*-Br	40	78
4	*p*-Br–Ph	*p*-OMe	50	75
5	*p*-NO_2–Ph	*o*-Br	30	85 (60)[c]

[a]Yields of isolated products.
[b]yield after 5th recycle of the catalyst.
[c]reaction was run at RT for 3–4 h.

We have also evaluated this catalytic system for one-pot synthesis of homoallylamines (table 2). As was the case with the allylation of aldehydes, addition of one equivalent of benzoic acid as an additive was necessary for rapid production of the homoallylamines. When the reaction of *p*-nitrobenzaldehyde was examined at room temperature, a 60% conversion in 3–4 h was observed. However, when the reaction was carried out at 40 °C, it was complete within 30 min and the desired product was isolated in 85% yield (entry 5, table 2) after flash chromatography (10% v/v ethyl acetate–hexane). A variety of aldehydes and amines have been examined in an effort to address the scope of this reaction, and the results are shown in table 2. All the aldehyde and amine combinations examined in table 2 showed good yields of the desired products within 50 min.

In summary, we have developed a new silica gel grafted bismuth triflate catalyst system for allylation of aldehydes and one-pot synthesis of homoallylamines with allyltributylstannane for the first time. The simple procedure for the preparation of the catalyst and easy recovery and reusability of the catalyst are expected to contribute to the development of the "green technology".

Acknowledgments

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