Polystyrene-Gallium Trichloride Complex: A Mild, Highly Efficient, and Recyclable Polymeric Lewis Acid Catalyst for Chemoselective Silylation of Alcohols and Phenols with Hexamethyldisilazane

Ali Rahmatpour,¹ Ali Vakili,² and Setare Azizian¹

¹*Polymer Science and Technology Division, Research Institute of Petroleum Industry, 14665-1137 Tehran, Iran*

²Institute for International Energy Studies, 196 774 3711, Tehran, Iran

Received 23 February 2013; revised 23 June 2013

ABSTRACT: Polystyrene-supported gallium trichloride ($PS/GaCl_3$) as a highly active and reusable heterogeneous Lewis acid effectively activates hexamethyldisilazane (HMDS) for the efficient silvlation of alcohols and phenols at room temperature. In this heterogeneous catalytic system, primary, secondary, and tertiary alcohols as well as phenols were converted to their corresponding trimethylsilyl ethers with short reaction times and high yields under mild reaction conditions. The heterogenized catalyst is of high reusability and stability in the silulation reactions and was recovered several times with negligible loss in its activity or a negligible catalyst leaching, and also there is no need for regeneration. It is noteworthy that this method can be used for chemoselective silulation of different alcohols and phenols with high yields. © 2013 Wiley Periodicals, Inc. Heteroatom Chem 24:443-451, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21109

INTRODUCTION

Functional group protection is the heart of multifunctional synthesis of target molecules. One of the most popular reactions for masking hydroxyl functional groups is their transformation to silyl ethers [1]. Preparation of silyl ethers is usually carried out by the treatment of alcohols with a variety of silylating agents, such as chlorotrimethylsilane [2], allylsilane [3], and hexamethyl disiloxane [4] in the presence of stoichiometric amount of an organic base, such as imidazole [5], N,N-diisopropylethylamine [6], and 4-(*N*,*N*-dimethylamino)pyridine [7]. However, these base-catalyzed silvlation methods have serious disadvantages since careful extraction and separation of ammonium salts formed as a by-product are time consuming and difficult processes. An alternative silvlating reagent for the preparation of silvl ethers from hydroxyl compounds is hexamethyldisilazane (HMDS), which is an inexpensive and commercially available reagent and gives ammonia as the only by-product. Even though the handling of this reagent is convenient, the main drawback of HMDS is its poor silvlating property, which demands relatively high catalyst loading, [15] high temperature, and long reaction times. A variety of catalysts such as ZnCl₂ [8], LiClO₄ [9], I₂ [10], (CH₃)₃SiCl

Correspondence to: Ali Rahmatpour; e-mail: rahmatpoura@ ripi.ir.

 $[\]ensuremath{\textcircled{}^{\circ}}$ 2013 Wiley Periodicals, Inc.

[11], Fe(HSO₄)₃ [12], Al(HSO₄)₃ [13], InBr₃ [14], Fe(CF₃CO₂)₃ [15], zirconium sulfophenyl phosphonate [16], $CuSO_4 \cdot 5H_2O$ [17], $Cu(OTf)_2$ [18], H₃PW₁₂O₄₀ [19], K-10 montmorillonite [20], sulfonic acid-functionalized nanoporous silica [21], zirconyl triflate [22], LaCl₃ [23], Mg(OTf)₂ [24], poly(N-bromobenzene-1,3-disulfonamide) and N, N, N', N'-tetrabromobenzene-1,3-disulfonamide [25], $(n-Bu_4N)Br$ [26], $[Ti(salophen)(OTf)_2]$ [27], Fe₃O₄ [28], H- β zeolite [29], ³⁰P/S-Bi [30], silica chloride [31], trichloroisocyanuric acid (TCCA) [32], alumina-supported heteropolyoxometalates [33], etc. [34] have been used to activate HMDS for the silvlation reaction. Even though these catalytic systems enhance the ability of HMDS for the silylation, some of these catalysts or activators require long reaction times, drastic reaction conditions or tedious workups, and excess amount of reagent. Hence, introduction of new protocols using stable, cost-effective, recyclable and non-corrosiveness catalysts with high efficiency are of great demand.

Increasing awareness of the environmental costs of traditional acid-catalyzed chemical transformations, in terms of the removal of toxic metals from the waste stream as well as the potential to control costs via catalyst recovery and recycling, has created an opportunity for new solid acid-based approaches for many important laboratory and industrial reactions [35–37]. In recent years, there have been intense efforts to replace these catalysts with ecofriendly reusable heterogeneous catalysts. Immobilization of catalysts on solid support improves the stability, hygroscopic properties, handling, and reusability of catalysts that all factors are important in industry and consequently the supported catalysts offer simpler and more environmentally benign alternatives than do their homogeneous counterparts [38,39]. A large number of polymer-supported Lewis acid catalysts have been prepared by immobilization of the catalysts on polymer via coordination or covalent bonds [40]. Such polymeric catalysts are usually as active and selective as their homogeneous or solution-phase counterparts while having the distinguishing characteristics of being easily separable from the reaction mixture, recyclability, easier handling, nontoxicity, enhanced stability, and improved selectivity in various organic reactions. Polystyrene is one of the most widely studied heterogeneous and polymeric supports due to its environmental stability and hydrophobic nature that protects water-sensitive Lewis acids from hydrolysis by atmospheric moisture until it is suspended in an appropriate solvent where it can be used in a chemical reaction [41]. It is well known that gallium trichloride is a strong Lewis acid and an important



SCHEME 1 Trimethylsilylation of alcohols and phenols with HMDS catalyzed by $PS/GaCl_3$.

catalyst in organic transformations. However, it easily hydrolyzes in air, so that its use, storage, and separation from a reaction mixture are inconvenient and difficult. Polystyrene-supported gallium chloride, PS/GaCl₃, which is a tightly bound and stable complex between anhydrous GaCl₃ and polystyrenedivinylbenzene copolymer beads, has been described for the first time by Ruicheng and Shuojian [42]. The use of the PS/GaCl₃ complex catalyst has several advantages over conventional Lewis acid catalyst such as its cost-effectiveness, ease of handling, recyclability, and tunable Lewis acidity.

In continuation of our recent works on the preparation and use of polymeric Lewis acid catalysts in synthetic transformations [43–46], in this work we found that polystyrene-supported gallium trichloride PS/GaCl₃ can be used as a stable, highly active, and reusable heterogeneous Lewis acid catalyst for the highly efficient o-silylation of a variety of alcohols and phenols using readily available HMDS (Scheme 1).

RESULTS AND DISCUSSION

Preparation of PS/GaCl₃ Complex

By considering the excellence of polystyrenedivinylbenzene (5-7%) copolymer beads (PS) as an effective supporting material for immobilization of Lewis acid previously reported [43, 44, 46] by our group, we decided to use PS beads as a support for the heterogenization of gallium trichloride. PS/GaCl₃ was prepared by addition of anhydrous gallium trichloride to polystyrene (5-7% divinylbenzene) in carbon disulfide under reflux conditions. The loading capacity of the polymeric catalyst obtained by the gravimetric method and checked by the atomic absorption technique was 0.391 mmol GaCl₃/g of complex beads catalyst [47, 48]. The UV spectrum of the solution of the PS-GaCl₃ complex in CS_2 showed a new strong band at 470 nm, which is due to the formation of a stable $\pi \rightarrow p$ type coordination complex between the benzene rings in the polystyrene carrier with gallium trichloride. The IR spectrum of PS/GaCl₃ showed new absorption peaks due to the C–C stretching vibration and the C–H bending vibration of the benzene ring at 1500–1560 and 400–800 cm⁻¹, by which complex formation was demonstrated. The structure of the PS-GaCl₃ complex is similar to that of the PS—AlCl₃ complex as suggested by Neckers and co-workers [49], because the Lewis acid GaCl₃ is complexed with the benzene rings of the polystyrene and the GaCl₃ is stabilized due to the decreased mobility of the benzene rings hindered by the long polystyrene chain. The PS—GaCl₃ complex is a nonhygroscopic, watertolerant, and especially stable species. In addition, this polymeric catalyst is easy to prepare, stable in air for a long time (over 1 year) without any change, easily recycled and reused without appreciable loss of its activity.

*Trimethylsilylation of Alcohols and Phenols with HMDS Catalyzed by PS/GaCl*₃

To study the feasibility of the PS/GaCl₃-catalyzed trimethylsilylation reaction, the reaction of benzyl alcohol (1 equiv) with HMDS (0.6 equiv) was selected as a model to screen the best conditions. The swelling property of cross-linked resin (PS) in organic solvents is an important factor for effective solid phase reactions [50]. To choose the reaction media, we examined different solvents such as toluene, tetrahydrofuran, acetonitrile, water, acetone, and methylenechloride. The results are summarized in Table 1. Among the tested solvents, the highest yield was obtained in CH₂Cl₂ (Table 1, entry 10). CH_2Cl_2 was chosen as the solvent system for this conversion, because of its swellability with the polymer network of the catalyst and miscibility with the substrates, allowing the metal particles located inside the polymer matrix to effect the catalvsis. No reaction occurred when H₂O was used as a solvent (Table 1, entry 5), because of the aggregation of the catalyst caused by its hydrophobic nature, leading to inadequate access of substrates to the active sites of the catalyst [51]. In addition, we further studied the influence of the amount of PS/GaCl₃ on the reaction yields. In the presence of 6, 4, 2, and 1 mol% PS/GaCl₃, the corresponding yields were 97, 88, 58, and 34%, respectively (Table 1, entries 7-10). The results show that 6 mol% of PS/GaCl₃ was sufficient to catalyze the reaction and excessive amount of catalyst did not increase the yields (Table 1, entry 11). Blank experiment in the absence of catalyst showed that the reaction was very sluggish to give only 8% the corresponding silvl ether after 60 min (Table 1, entry 6). The key role played by the Lewis acidity of the heterogeneous catalyst PS/GaCl₃ was proved by employing the polystyrene beads (Table 1, entry 12) and the GaCl₃-toluene

TABLE 1ReactionConditionsOptimizationintheTrimethylsilylation ofBenzylAlcoholwithHMDSCatalyzedbyPS/GaCl₃atRoomTemperature^a

Entry	Solvent	Catalyst (mol %)	Time (min)	Yield⁵ (%)
1	Toluene	6	30	22
2	THF	6	30	28
3	CH₃COCH₃	6	30	62
4	CH₃CN	6	30	67
5	H ₂ O	6	30	NR^{c}
6 ^d	CH_2CI_2	_	60	< 8 ^d
7	CH_2CI_2	1	25	34
8	CH ₂ Cl ₂ 2 25 58			
9	CH_2CI_2	4	25	88
10	CH_2CI_2	6	20	97
11	CH ₂ Cl ₂	8	20	97
12 ^e	CH ₂ Cl ₂	_	20	NR
13 ^f	CH_2CI_2	_	20	68
14 ^{<i>g</i>}	CH_2CI_2	6	10	NR
15 ^{<i>h</i>}	CH_2CI_2	6	20	69

^aReaction conditions: benzyl alcohol (1 mmol), HMDS (0.6 mmol), solvent (3 mL).

^bIsolated yield.

^cNR: No reaction.

^dNR: No catalyst and GC yield.

^ePS was used as a catalyst.

^tThe toluene-GaCl₃ complex was used as a catalyst.

^gCatalyst was filtered after 10 min.

^hPS/AICl₃ (0.1 mmol, 0.47 mmol AICl₃/g) was used as a catalyst.

complex (Table 1, entry 13) as catalysts. In fact, while in the former case no reaction occurred, which indicated that polystyrene itself did not promote the reaction, in the latter, the desired product was isolated in low yield 68% (Table 1, entry 13). Also, PS/GaCl₃ was found to be a more effective catalyst than PS/AlCl₃ for trimethylsilylation of benzyl alcohol under identical conditions (Table 1, entry 15).

The lifetime and leaching of active sites into the reaction mixture are important issues to consider when heterogeneous and metal-supported catalysts are used, particularly for practical applications of the reaction. Our preliminary investigations demonstrated that the PS/GaCl₃ catalyst (a stable π complex) is very stable to air and moisture. To rule out the presence of concurrent homogeneous catalysis, the silvlation reaction of benzyl alcohol was carried out in methylene chloride in which the catalyst PS/GaCl₃ was filtered after 10 min and the resulting clear solution was stirred for an additional 1 h in the absence of the catalyst. Further treatment of the filtrate under similar reaction condition did not proceed significantly (Table 1, entry 14). On the other hand, after each run the filtrates were used for the determination of catalyst leaching (gallium content), which showed a negligible release of $GaCl_3$ by atomic absorption or inductively coupled plasma measurement. The capacity of the catalyst after five

Entry	ROH	Substrate/HMDS	Product (TMS-ether)	Time (min)	Yield ^b (%)	Reference
1	C ₆ H ₅ CH ₂ OH	1:0.6	C ₆ H ₅ CH ₂ OTMS	20	97	[22]
2	<i>p</i> -(Cl)C ₆ H ₄ CH ₂ OH	1:0.6	p-(Cl)C ₆ H ₄ CH ₂ OTMS	25	95	[22]
3	m-(NO ₂)C ₆ H ₄ CH ₂ OH	1:0.7	$p-(NO_2)C_6H_4CH_2OTMS$	50	89	[20–22]
4	p-(CH ₃)C ₆ H ₄ CH ₂ OH	1:0.6	p-(CH ₃)C ₆ H ₄ CH ₂ OTMS	20	97	[20–22]
5	p-(OCH ₃)C ₆ H ₄ CH ₂ OH	1:0.6	p-(OCH ₃)C ₆ H ₄ CH ₂ OTMS	20	98	[20–22]
6	3,4-(OCH ₃) ₂ C ₆ H ₃ CH ₂ OH	1:0.6	3,4-(OCH ₃)C ₆ H ₃ CH ₂ OTMS	20	98	[20-22,25]
7	C ₆ H ₅ NHCH ₂ CH ₂ OH	1:0.6	C ₆ H ₅ NHCH ₂ CH ₂ OTMS	20	96	[25,27]
8	$C_6H_5CH_2CH_2CH_2OH$	1:0.6	$C_6H_5CH_2CH_2CH_2OTMS$	20	97	[25,27]
9	$n-CH_3(CH_2)_6CH_2OH$	1:0.6	n-CH ₃ (CH ₂) ₆ CH ₂ OTMS	25	96	[20-22]
10	n-CH ₃ (CH ₂) ₅ CH ₂ OH	1:0.6	$n-CH_3(CH_2)_5CH_2OTMS$	25	96	[20-22,25]
11	$CH_3(CH_2)_3CH(OH)CH_3$	1:0.6	CH ₃ (CH ₂) ₃ CH(OTMS)CH ₃	35	94	[25,27]
12	(CH ₃) ₂ CHOH	1:0.7	(CH ₃) ₂ CHOTMS	35	92	[20–22]
13	$C_6H_5CH(CH_3)CH_2OH$	1:0.6	C ₆ H ₅ CH(CH ₃)CH ₂ OTMS	30	94	[20-22, 25]
14	$C_6H_5CH(CH_3)OH$	1:0.7	$C_6H_5CH(CH_3)$ OTMS	45	93	[25, 32]
15	$C_6H_5C(CH_3)_2$ OH	1:0.8	$C_6H_5C(CH_3)_2$ OTMS	55	91	[20-22]
16	ОН — ОН	1.0 2	-OTMS	50	92	[22 25 32]
17		1.0.8		45	91	[20-22 25]
18		1.0.9		60	89	[20-22]
19	$p_{\rm c}({\rm OCH}_{2})C_{\rm c}{\rm H}_{4}{\rm OH}$	1.0.7	$p_{\rm c}({\rm OCH}_{2})C_{\rm c}{\rm H}_{4}{\rm OTMS}$	45	92	[20-22 27]
20	p-(CH ₂)C _e H ₄ OH	1.0.7	p-(CH ₂)C _e H ₄ OTMS	35	92	[20-22 25]
21	p-(isopropyl)C _e H ₄ OH	1:0.7	p-(isopropyl)C _e H ₄ OTMS	35	91	[20-22,27]
22	p-(NO ₂)C ₆ H ₄ OH	1:1	p-(NO ₂)C ₆ H ₄ OTMS	80	NR ^c	[20-22]
	OH		OTMS			[_0]
23		1:0.9		80	88	[20–22]
24	HOCH ₂ (CH ₂) ₃ CH ₂ OAc	1:0.6	SMTOCH ₂ (CH ₂) ₃ CH ₂ OAc	25	92	[32]
25	HOCH ₂ (CH ₂) ₆ CH ₂ OBn	1:0.6	SMTOCH ₂ (CH ₂) ₆ CH ₂ OBn	25	93	
26	HOCH ₂ (CH ₂) ₆ CH ₂ OBz	1:0.6	SMTOCH ₂ (CH ₂) ₆ CH ₂ OBz	25	93	[32]
27	HOCH ₂ (CH ₂) ₃ CH ₂ OTs	1:0.6	SMTOCH ₂ (CH ₂) ₃ CH ₂ OTs	25	91	
28	$C_6H_5CH_2NH_2$	1:0.6	_	90	NR	[52]
29	$C_6H_5CH_2SH$	1:0.6	-	90	NR	[52]

TABLE 2 Trimethylsilylation of Alcohols and Phenols Catalyzed by PS/GaCl_{3²} at Room Temperature

^aAll reactions were carried out in CH₂Cl₂ (3 mL) in the presence of PS/GaCl₃ (0.06 mmol) at room temperature.

^bGc yields. ^cNR: No reaction.

"INR: No reaction.

uses was 0.383 mmol of GaCl₃ per gram. Therefore, we may conclude that PS/GaCl₃ is stable and no significant leaching of Lewis acid moieties is operating under our reaction conditions and any gallium species that leached into the reaction mixture is not an active homogeneous catalyst and that the observed catalysis is truly heterogeneous in nature.

Furthermore, we carried out the reactions between HMDS and various alcohols to explore the reaction scope of PS/GaCl₃-catalyzed trimethylsilylation; the results are summarized in Table 2. As can be seen, all reactions proceeded very cleanly (checked by GC) in good to excellent yields. A broad selection of alcohols, including primary (benzylic and linear ones; Table 2, entries 1–10, 13), secondary (including aliphatic and aromatic alcohols; Table 2, entries 11, 12, 14, 16), tertiary and allylic alcohols, were converted to their corresponding trimethylsilyl-ethers (TMS-ethers) successfully at room temperature (Table 2). Benzyl alcohol and most of its vari-

ous derivatives undergo the silvlation with excellent yields (Table 2, entries 1-6). Only *m*-nitrobenzyl alcohol reacts rather slowly (50 min) with reduced vield (89%) (entry 3). This could be due to the electron-withdrawing power of the nitrosubstituent. Anilinoethanol gives the o-silylation product with excellent yield (Table 2, entry 7). It is noteworthy that in the case of both tertiary and allylic alcohols, which are acid-sensitive alcohols, due to the mild reaction conditions, no rearrangement or dehydration side products were observed at all, and they were also converted to their corresponding TMS-ethers in high yields (Table 2, entries 15, 17). We were then interested in whether the same catalyst could be employed for trimethylsilylation of phenolic compounds. By following identical reaction procedures described for alcohols, various phenols (Table 2, entries 18-23) were smoothly converted into the corresponding TMS-ethers in good yields. However. compared with aliphatic

TABLE 3 Selective Silylation Reactions of Alcohols and Phenols Catalyzed by $PS/GaCl_3^a = R^1OH + R^2OH + R^2OH + R^2OSiMe_3 = R^1OSiMe_3 + R^2OSiMe_3$

				Yield (%) ^t	0
Entry	Substrate 1	Substrate 2	Time (min)	TMS-ether 1	TMS-ether 2
	OH				
1	он	СН2ОН	20	4	93
2	ОН	СН2ОН	20	2	93
3		СН2ОН	20	0	93
4	сон Сон	СН2ОН	20	4	92
5		СН2ОН	20	3	90
6 7 8	→ OH HSCH₂ H₂N CH	CH ₂ OH	20 20 20	4 HSCH2CH2OTMS H2N CH2CH2OTMS	91 100 100
9	CH₃COC	$\bar{H}_2C\bar{H}_2OH$	20	CH ₃ COCH ₂ CH ₂ OTMS	100

^aAll reactions were carried out in CH₂Cl₂ in the presence of PS/GaCl₃ (6 mol%, 0.06 mmol) at room temperature. ^bYields based on GC and NMR.

alcohols, aromatic alcohol substrates needed somewhat higher amounts of HMDS and longer reaction times to obtain the silvlation products with reasonable yield. For example, 2-naphthol offered 88% vield in 80 min reaction time (Table 2, entry 23). As can be seen, unsubstituted phenol requires a longer reaction time and phenol whose benzene ring was substituted with a strong electron-donating group reacted quickly with excellent yield (Table 2, entries 18–21). However, *p*-nitrophenol fails to produce silylation product (Table 2, entry 22). This result may indicate that the electron-withdrawing ability of the nitro group could reduce the electron density on the oxygen atom that prohibits the silvlation. We then turned our attention to whether the same catalyst could be useful for trimethylsilylation of substrates containing other protecting groups. We observed that various protected alcohols (Table 2, entries 24-27) containing protecting groups such as acetyl, benzyl, benzoyl, and tosyl were smoothly converted into the corresponding TMS-ethers without affecting the other protecting groups. Timethylsilylation of the other types of hydrogen-labile substrates such as amines and thiols under similar reaction conditions

did not proceed at all (Table 2, entries 28, 29). The lack of reactivity can be ascribed to the higher affinity of the silicon atom of HMDS toward the oxygen of the hydroxyl group than the nitrogen and sulfur (N—H and S—H bonds) of amine and thiol, respectively [52]. These data demonstrate that HMDS does not interact with amine and thiols under the present conditions.

Selectivity of the catalysts for chemical transformations is important, especially, when the catalyst is used in multistep synthesis. The difference in reactivity of the PS/GaCl₃ catalyst toward alcohols gave us the impetus to study chemoselective reactions. When an equimolar mixture of benzyl alcohol and secondary or tertiary alcohols or phenols was reacted with HMDS under the same reaction conditions, only the benzyl alcohol was converted predominantly to TMS-ether products (Table 3, entries 1–6). This heterogeneous catalytic protocol was utilized successfully in the selective silvlation of the hydroxyl group in the presence of other functional groups in the same molecule (Table 3). The present method tolerates the presence of thiol (entry 7), amine (entry 8), and enolizable carbonyl group (entry 9).



SCHEME 2 Plausible mechanism for the silylation of alcohol and phenols with HMDS catalyzed by PS/GaCl₃.

The plausible reaction pathway has been shown in Scheme 2. In this mechanism, it is suggested that the Lewis acid-base interaction between $PS/GaCl_3$ and the nitrogen in HMDS polarizes the N—Si bond of HMDS and a reactive silylating agent **1** is produced, which rapidly interacts with alcohol to give the *O*—silyl ether and complex **2**. This complex **2** effectively silylates the another molecule of alcohol to produce the silyl derivative. Finally, unstable complex **3** releases the ammonia and catalyst which reenters to the catalytic cycle. The fast evolution of ammonia gas (odor and litmus paper) is a good indication for the proposed mechanism.

To show the efficiency and applicability of the present method, the catalytic activity of $PS/GaCl_3$ was compared with that of some reported cata-

lysts in the literature, the results are summarized in Table 4. The results have been compared with respect to the reaction times, catalyst loading, and yields. As demonstrated in Table 4, PS/GaCl₃ is an equally or more efficient catalyst for this trimethylsilylation reaction in terms of the yield and reaction rate.

Catalyst Reusability

Finally, the reusability of the catalyst was also checked using multiple silylation of benzyl alcohol with HMDS under the same reaction conditions described in the general procedure. At the end of each of the repeated reactions, the catalyst was filtered, washed exhaustively with methylene chloride and diethyl ether, respectively, and dried before using with fresh benzyl alcohol and HMDS. The catalyst was consecutively reused five times with negligible loss in its activity, and there is no need for regeneration (Table 5).

In conclusion, in this paper, a simple, mild, efficient, and chemoselective method for trimethylsilylation of alcohols and phenols using stable and heterogeneous polystyrene-supported gallium trichloride is reported. The short reaction times, high to excellent yields, low cost, easy preparation, and handling of the polymeric Lewis acid catalyst are the advantages of the present method. In addition, the use of water-tolerant PS/GaCl₃ has resulted in a reduction in the unwanted and hazardous waste and minimum amount of product contamination with metal that is produced during conventional homogeneous processes. Most importantly, the workup is

TABLE 4 PS/GaCl₃-Catalyzed Trimethylsilyl Protection of Alcohols in Comparison with Other Literature

Entry	Catalyst (mol%)	Conditions	Time	Ref.
1	LaCl ₃ (10)	CH ₂ Cl ₂ /r.t.	3–5 h	[23]
2	Sulfonic acid nanoporous silica (3)	$CH_2 CI_2/r.t.$	80–120 min	[21]
3	$Fe(F_3CCO_2)_3$ (2)	Neat/r.t.	5 min–2 h	[15]
4	$H_3 PW_{12}O_{40}(1)$	Neat/55–60°C	6–135 min	[19]
5	$H-\beta$ zeolite (19 mg)	Neat/80°C	5–30 h	[29]
6	K-10 montmorillonite (100 mg)	$CH_2CI_2/r.t.$	24–60 min	[20]
7	Zirconium sulfophenyl phosphonate (50 mg)	$CH_2 CI_2/r.t.$	1–20 h	[16]
8	Poly(N-bromobenzene-1,3-disulfonamide) (0.2 g)	$CH_2 CI_2/r.t.$	0.25–3.5 h	[25]
9	TCCA (10)	$CH_2 CI_2/r.t.$	1.5–4 h	[32]
10	Silica chloride	CH ₃ CN /reflux	12–90 min	[31]
11	³⁰ P/Si-Bi (50 mg)	$CH_2Cl_2/r.t.$	10–55 min	[30]
12	$CuSO_4.5H_2O(10)$	CH ₃ CN/reflux	3.5–35 h	[17]
13	$Fe(HSO_4)_3$ (0.3 mmol)	CH ₃ CN/reflux	0.25–2.7 h	[12]
14	AI(HSO ₄) ₃	<i>n</i> -Hexane/reflux	0.3–4 h	[13]
15	$Mg(OTf)_2(1)$	Neat/r.t.	0.7–2 h	[24]
16	Alumina-supported heteropolyoxometalates (100 mg)	Toluene/85°C	60–120 min	້ອວງ
17	PS/GaCl ₃ (6)	$CH_2Cl_2/r.t.$	20–80 min	This work

Abbreviation: r.t., room temperature.

TABLE 5Reusability of ${}^{a}PS/GaCl_{3}$ in the Trimethylsilylationof Benzyl Alcohol with HMDS^b

Run	TMS-ether (%) ^c	Time (min)
1	97	20
2	96	20
3	94	20
4	92	20
5	90	25

 $^{a}\mbox{The capacity of the catalyst after five uses was 0.383 mmol <math display="inline">\mbox{GaCl}_{3}$ per gram.

^bReaction conditions: benzyl alcohol (1 mmol), HMDS (0.6 mmol), PS/GaCl₃ (0.06 mmol), and CH₂Cl₂ (3 mL).

^cIsolated yield.

reduced to a mere filtration and evaporation of the solvent. Finally, this catalytic system showed a good catalytic activity in these reactions and this polymeric catalyst can be recovered unchanged and used again at least five times with negligible loss in its activity.

EXPERIMENTAL

Materials and Methods

All chemical reagents and solvents were obtained from Merck (Germany) or Fluka (Switzerland) and were used without further purification. Cross-linked polystyrene (5–7% divinylbenzene, mesh size: 25–70) was prepared via suspension polymerization as reported in the literature [43, 44]. PS/AlCl₃ was also prepared as previously reported [43]. FT-IR spectra of the samples were recorded from 400 to 4000 cm⁻¹ on a Unicam Matteson 1000 spectrophotometer. ¹H, ¹³C NMR spectra were recorded on a Bruker DPX-250 Avance spectrometer (Karlsruhe, Germany) at 250.13 MHz. Mass spectra were recorded on Shimadzu GC-MS QP 1000 EX. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2-m column packed with silicon DC-200 or carbowax 20 M. The capacity of the catalyst was determined by the gravimetric method (Mohr titration method) and atomic absorption technique using a Philips atomic absorption instrument. Reaction monitoring and purity determination of the products were accomplished by TLC on silica gel polygram SILG/UV₂₅₄ plates.

Preparation of Polystyrene-Supported Gallium Trichloride (PS/GaCl₃)

Anhydrous GaCl₃ (4.50 g) was added to polystyrene (5-7% divinylbenzene, mesh size: 25-70, 40 g) in carbon disulfide (5 mL) as the reaction medium. The mixture was stirred using a magnetic stirrer un-

der reflux condition for 1 h, cooled, and then water (50 mL) was cautiously added to hydrolyze the excess GaCl_{3.} The mixture was stirred until the bright red color disappeared, and the polymer became yellow. The polymer beads were collected by filtration and washed with water (300 mL) and then with ether (30 mL) and chloroform (30 mL). The catalyst was dried in a vacuum oven overnight at 50°C before use. The chlorine content of PS/GaCl₃ was 4.17% analyzed by the Mohr titration method [47], and the loading capacity of GaCl₃ on the polymeric catalyst or the amount of GaCl₃ complexed with polystyrene was calculated to be 0.391 mmol/g [48].

General Experimental Procedure for Trimethylsilylation of Alcohols and Phenols with HMDS Catalyzed by the PS/GaCl₃ Complex

In a round-bottom flask equipped with a magnetic stirrer, to a solution of alcohol or phenol (1 mmol) and HMDS (0.6-0.9 mmol) in methylene chloride (3 mL), PS/GaCl₃ (0.06 mmol) was added and the resulting mixture was stirred at room temperature for an appropriate time. The progress of the reaction was monitored by GC or TLC (*n*-hexane/EtOAc, 9:1). After completion of the reaction, the catalyst was filtered and washed with methylene chloride $(2 \times 10 \text{ mL})$ and the filtrate concentrated on a rotary evaporator under reduced pressure to afford the crude product. Further purification was achieved by column chromatography on silica gel (Merck, 100– 200 mesh) to give the desired product. The spent polymeric catalyst from different experiments was combined, washed with ether, and dried overnight in a vacuum oven and reused. ¹H and ¹³C NMR and GC-MS data for new products are given below (Table 2, entries 6, 7; Table 3, entry 9). ¹H and ¹³C NMR and MS data for the known TMSether products are the same as literature values [9, 20–22, 25, 27, 32, 53].

The Spectral Data for Selected Products

(3,4-Dimethoxybenzyloxy)trimethylsilane (Table 2, entry 6). IR (neat) cm⁻¹: ν = 2955, 2898, 1590, 1457, 1249, 1126, 1097, 870, 837, 751.¹H NMR (250 MHz, CDCl₃, Me₄ Si): δ = 0.00 (s, 9H, -Si(CH₃)₃), 3.65 (s, 3H, -OCH₃), 3.67(s, 3H, -OCH₃), 4.45 (s, CH₂Ar), 6.38 (s, 3H, Ar-H). ¹³C NMR (62.89 MHz, CDCl₃, Me₄Si): δ = 0.00, 56.25 (OCH₃), 61.1 (OCH₃), 65.1 (CH₂Ar), 104.0 (Ar-C), 137.3 (Ar-C), 153.5 (Ar-C). GCMS: *m*/*z* = 270.1 [M⁺]. *N*-((2-*Trimethylsilyloxy*)*ethyl*)*aniline* (*Table 2*, *entry* 7). ¹H NMR (250 MHz, CDCl₃, Me₄ Si): $\delta =$ 0.00 (s, 9H, —Si(CH₃)₃)), 3.09 (t, *J* = 7.6 Hz, 2H), 3.64 (t, *J* = 7.6 Hz, 2H), 3.88 (s, 1H), 6.48–6.61 (m, 3H), 7.00–7.08 (m, 2H). ¹³C NMR (62.89 MHz, CDCl₃, Me₄Si): $\delta = 0.5$, 45.9, 61.0, 113.2, 117.5, 129.2, 148.3. GCMS: *m*/*z* = 209 [M⁺].

4-(*Trimethylsilyloxy*)*butan-2-one* (*Table 3, entry* 9). IR (neat) cm⁻¹: $\nu = 2958$, 2898, 1715, 1358, 1250, 1169, 1097, 877, 837, 750. ¹H NMR (250 MHz, CDCl₃, Me₄Si): $\delta = 0.04$ (s, 9H, $-Si(CH_3)_3$), 2.07 (s, 3H, CH₃CO–), 2.5 (t, J = 6.4 Hz, 2H, $-COCH_2$.), 3.7 (t, J = 6.4 Hz, 2H, $-CH_2O-Si$). ¹³C NMR (62.89 MHz, CDCl₃, Me₄Si): $\delta = 0.4$, 30.8, 46.5, 58.1, 207.8 (CO). GCMS: m/z = 161 [M⁺].

Catalyst Recovery and Reuse

The reusability of the catalyst was checked in the multiple trimethylsilylation of benzyl alcohol with HMDS. At the end of each reaction, the solvent was evaporated, ether (Et_2O , 10 mL) was added, and the catalyst was filtered. The recovered catalyst was used with fresh benzyl alcohol, HMDS, and CH_2Cl_2 .

ACKNOWLEDGMENT

The author is grateful to Tabriz Petrochemical Complex for providing polystyrene.

REFERENCES

- [1] Wuts, P. G. M.; Greene, T. W. Protective Groups in Organic Synthesis, 4th ed.; Wiley: New York, 2007.
- [2] Bandgar, B. P.; Chavare, S. N.; Pandit, S. S. J Chin Chem Soc 2005, 52(1), 125.
- [3] Morita, T.; Okamoto, Y.; Sakurai, H. Tetrahedron Lett 1980, 21, 835.
- [4] Cooper, B. E. Chem Ind 1978, 107, 794.
- [5] Corey, E. J.; Venkateswarlu, A. J Am Chem Soc 1972, 94, 6190.
- [6] Lombardo, L. Tetrahedron Lett 1984, 25, 227.
- [7] Chaudhary, S. K.; Hernandez, O. Tetrahedron Lett 1979, 20, 99.
- [8] Firouzabadi, H.; Karimi, B. Synth Commun 1993, 23, 1633.
- [9] Saidi, M. R.; Azizi, N. Organometallics 2004, 23, 1457.
- [10] Karimi, B.; Golshani, B. J Org Chem 2000, 65, 7228.
- [11] Gauttret, P.; EI-Ghamarti, S.; Legrand, A.; Coutrier, D.; Rigo, B. Synth Commun 1996, 26, 707.
- [12] Shirini, F.; Zolfigol, M. A.; Abri, A. R. Monatsh Chem 2008, 139, 17.
- [13] Shirini, F.; Abedini, M. A. Bull Chem Soc Japan 2005, 78, 1982.
- [14] Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Baishya, G.; Venkat Narsaiah, A. Synthesis 2006, 3831.

- [15] Firouzabadi, H.; Iranpoor, N.; Jafari, A. A.; Jafari, M. R. J Organomet Chem 2008, 693, 2711.
- [16] Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. Synth Commun 1999, 29, 541.
- [17] Akhlaghinia, B.; Tavakoli, S. Synthesis 2005, 1775.
- [18] Firouzabadi, H.; Iranpoor, N.; Sobhani, S.; Ghassamipour, S.; Amoozgar, Z. Tetrahedron Lett 2003, 44, 891.
- [19] Firouzabadi, H.; Iranpoor, N.; Amani, K.; Nowrouzi, F. J Chem Soc, Perkin Trans 2002, 1, 2601.
- [20] Zhang, Z. H.; Li, T. S.; Yang, F.; Fu, C. G. Synth Commun 1998, 28, 3105.
- [21] Zareyee, D.; Karimi, B. Tetrahedron Lett 2007, 48, 1277.
- [22] Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Chahardah Cheric, S.; Tavakoli, Z. J Organomet Chem 2008, 693, 2041.
- [23] Narsaiah, A. V. J Organomet Chem 2007, 692, 3614.
- [24] Firouzabadi, H.; Iranpoor, N.; Sobhani, S.; Ghassamipour, S. J Organomet Chem 2004, 689, 3197.
- [25] Ghorbani-Vaghei, R.; Zolfigol, M. A.; Chegeny, M.; Veisi, H. Tetrahedron Lett 2006, 47, 4505.
- [26] Shirini, F.; Abedini, M. J Iran Chem Soc 2008, 5, 587.
- [27] Yadegari, M.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I. Polyhedron 2012, 31, 332.
- [28] Mojtahedi, M. M.; Abaee, M. S.; Eghtedari, M. Appl Organomet Chem 2008, 22, 529.
- [29] Tillu, V. H.; Jadhav, H.; Borate, H. B.; Wakharkar, R. D. ARKIVOC 2004, 14, 83.
- [30] Lee, S. H.; Kadam, S. T. Appl Organomet Chem 2011, 25, 608.
- [31] Shirini, F.; Zolfigol, M. A.; Abedini, M. Phosphorus Sulfur Silicon 2005, 180, 2299.
- [32] Khazaei, A.; Zolfigol, M. A.; Rostami, A. Catal Commun 2007, 8, 543.
- [33] Villabrille, P.; Romanellia, G.; Quarantab, N.; Vazquez, P. Appl Catal B: Environ 2010, 96, 379.
- [34] (a) Eshghi, H.; Rahimizadeh, M.; Ghadamyari, Z.; Shiri, A. Synth React Inorg Met-Org Nano-Met Chem 2012, 42, 1435; (b) Gharaati, S.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I. Polyhedron 2012, 35, 87; (c) Ghorbani-Choghamarani, A.; Norouzi, M. Chin J Catal 2011, 32, 595; (d) Hou, J. T.; Chen, H. L.; Zhang, Z. H. Phosphorus Sulfur Silicon Relat Elem 2011, 186, 88; (e) Jereb, M. Tetrahedron 2012, 68, 3861; (f) Rajabi, F.; R. Lugue, R.; Serrano-Ruiz, J. C. Chem Biodiversity 2012, 9, 1823; (g) Shirini, F.; Atghia, S. V.; Jirdehi, M. G. Catal Commun 2012, 18, 5; (h) Shirini, F.; Mamaghani, M.; Atghia, S. V. Appl Clay Sci 2012, 58, 67; (i) Shirini, F.; Mashhadi-Nejad, M. Phosphorus Sulfur Silicon Relat Elem 2012, 187, 376; (j) Yadollahi, B.; Mirkhani, V.; Tangestaninejad, S.; Karimian, D. Appl Organomet Chem 2011, 25, 83.
- [35] Olah, G. A.; Pradeep, S. I.; Prakash, G. K. S. Synthesis 1986, 513.
- [36] Clark, J. H. Acc Chem Res 2002, 35, 791.
- [37] Anastas, P. T.; Kirchhoff, M. M. Acc Chem Res 2002, 35, 686.
- [38] Clark, J. H. Catalysis of Organic Reactions by Supported Inorganic Reagents, VCH: Weinheim, Germany, 1994; p. 126.
- [39] Madhavan, M.; Jones, C. W.; Weck, M. Acc Chem Res 2008, 41(9), 1153.

- [40] Smith, K. Solid Supports and Catalysts in Organic Synthesis; Ellis Horwood: Chichester, UK, 1992.
- [41] Akela, A.; Moet, A. Functionalized Polymers and Their Applications; Wiley: New York, 1990, p. 11–15.
- [42] Ruicheng, R.; Shuojian, J.; Ji, S. J Macromol Sci Chem A 1987, 24(6), 669.
- [43] (a) Rahmatpour, A.; Aalaie, J. Heteroatom Chem 2011, 22, 85. (b) Rahmatpour, A.; Aalaie, J. Heteroatom Chem 2011, 22, 51.
- [44] Rahmatpour, A. Heteroatom Chem 2012, 23, 472.
- [45] Rahmatpour, A. Appl Organomet Chem 2011, 25(8), 585.
- [46] Rahmatpour, A. J Organomet Chem 2012, 712, 15.
- [47] Kolthoff, I. M.; Sandell, E. B. Textbook of Quantitative Inorganic Analysis; Macmillan: New York, 1965; p. 451.

- [48] Deshmukh, A. P.; Padiya, K. J.; Salunkhe, M. M. J Chem Res (S) 1999, 9, 568.
- [49] Neckers, D. C.; Kooistra, D. A.; Green, G. W. J Am Chem Soc 1972, 94, 9284.
- [50] Vaino, A. R.; Janda, K. D. J Combust Chem 2000, 2, 579.
- [51] Tamami, B.; Parvanak Borujeni, K. Catal Commun 2007, 8, 1191.
- [52] (a) Vorbruggen, H.; Krolikiewicz, K. Liebigs Ann Chem 1976, 746; (b) Vorbruggen, H.; Krolikiewicz, K.; Niedballa, U. Liebigs Ann Chem 1975, 988; (c) Cook, M. J.; Katritzkyand, A. R.; Linda, P. Adv Heterocycl Chem 1974, 17, 255; (d) Singer, R. A.; Dore, M. Org Process Res Dev 2008, 12, 1261.
- [53] Shaterian, H. R.; Shahrekipoor, F.; Ghashang, M. J Mol Catal A: Chem 2007, 272, 142.