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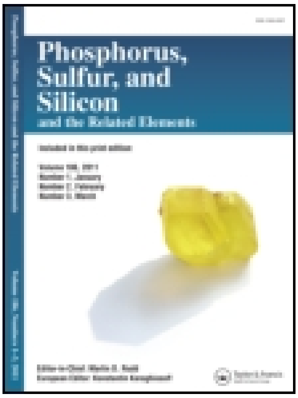

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Polystyrene and Silica Gel-Supported, $AlCl_3$-Catalyzed Preparation of Diaryl Sulfoxides from Arenes and Thionyl Chloride

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Published online: 24 Sep 2010.

To cite this article: Kaveh Parvanak Boroujeni (2010) Polystyrene and Silica Gel-Supported, $AlCl_3$-Catalyzed Preparation of Diaryl Sulfoxides from Arenes and Thionyl Chloride, Phosphorus, Sulfur, and Silicon and the Related Elements, 185:10, 2085-2091, DOI: 10.1080/10426500903496721

To link to this article: http://dx.doi.org/10.1080/10426500903496721

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Phosphorus, Sulfur, and Silicon, 185:2085–2091, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903496721

POLYSTYRENE AND SILICA GEL–SUPPORTED, $AlCl_3$-CATALYZED PREPARATION OF DIARYL SULFOXIDES FROM ARENES AND THIONYL CHLORIDE

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A simple, chemoselective, and efficient method has been developed for direct conversion of arenes to symmetrical diaryl sulfoxides using thionyl chloride in the presence of a catalytic amount of cross-linked polystyrene-supported aluminium chloride (Ps-$AlCl_3$) and silica gel–supported aluminium chloride (SiO_2-$AlCl_3$). These solid acid catalysts are stable and can be easily recovered and reused without appreciable change in their efficiency.

Keywords Arene; polystyrene; silica gel; sulfinylation; sulfoxide

INTRODUCTION

Sulfoxides are highly important intermediates in organic synthesis[1] and in the field of drugs and pharmaceuticals.[2,3] They often play an important role as therapeutic agents such as antihypertensive,[4] anthelmintic,[5] and cardiotonic agents.[6] Optically active sulfoxides have received much attention as important chiral auxiliaries in asymmetric synthesis[7] and in carbon–carbon bond forming reactions.[8] In addition, syntheses of diaryl sulfoxides provide a convenient route to triarylsulfonium salts, which are used as photoactive cationic initiators[9] and for the photogeneration of protonic acids in the lithographic resist field.[10] Usually, sulfoxides are prepared by indirect methods, which involve oxidation of sulfides,[11,12] reduction of sulfones,[13] and the reaction of organometallic reagents with sulfinic acid esters, mixed anhydrides, or sulfines.[14] A literature survey shows that less attention has been paid to the use of direct methods for the preparation of sulfoxides. Addition of aryl Grignard reagents to thionyl chloride,[14] the Friedel–Crafts sulfinylation of arenes with benzenesulfinyl chloride using a Lewis acid catalyst such as $AlCl_3$,[15] the reaction of arenes with FSO_3H-SbF_5 (Magic acid)/SO_2,[16] and the reaction of arenes with thionyl chloride in the presence of a catalyst such as trifluoromethane sulfonic acid,[17] scandium triflate,[18] ionic liquid,[19] heteropoly acid,[20] and sulfated zirconia[21] are some of the reported direct methods of preparation of diaryl sulfoxides. Except for a few, many of the above methods suffer from

Received 24 September 2009; accepted 18 November 2009.

Dedicated to the memory of Professor Ahmad Banihashemi.

The author thanks the Research Council of Shahrekord University for partial support of this work.

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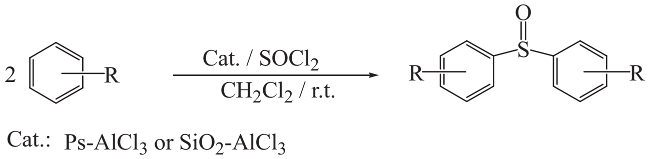
the drawbacks such as disturbance to other functional groups, less selectivity, the formation of a mixture of products containing sulfonium salts and chlorinated byproducts along with desired sulfoxide, environmental pollution, tedious work-up, a need for stoichiometric or excess amounts of catalyst in some reactions, and the use of moisture-sensitive, expensive, hazardous, difficult to handle, or unreusable catalysts. In view of these, the search for finding a cost effective, mild, and simple chemoselective protocol for the synthesis of sulfoxides is still relevant.

In recent years, the use of heterogeneous catalysts has received considerable attention in different areas of organic synthesis. The high selectivity, nontoxicity, noncorrosiveness, easy separation from the reaction media, recyclability, moisture and air tolerance, and easier handling make the use of heterogeneous catalysts attractive alternatives to conventional homogeneous catalysts.[22,23] Although the catalytic applications of heterogeneous catalysts for organic synthesis have been well established, relatively few examples are reported on the use of polymer-supported Lewis acid catalysts.[24]

Over the last several years, Ps-$AlCl_3$ and SiO_2-$AlCl_3$ have been reported to catalyze Friedel–Crafts acylation of aromatic compounds.[25,26] In a previous study, we also reported the use of Ps-$AlCl_3$ and SiO_2-$AlCl_3$ as remarkably efficient heterogeneous catalysts for the Friedel–Crafts sulfonylation of arenes.[27] Along this line, we report in this article that Ps-$AlCl_3$ and SiO_2-$AlCl_3$ are also highly efficient and chemoselective catalysts for the electrophilic sulfinylation of arenes with thionyl chloride under mild reaction conditions (Scheme 1).

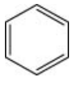
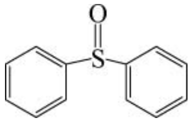
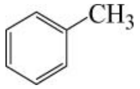
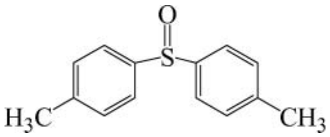
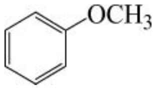
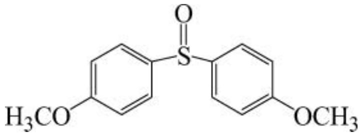
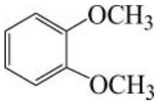
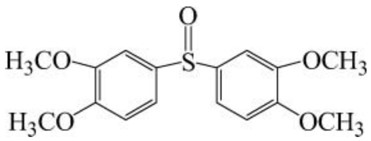
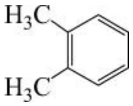
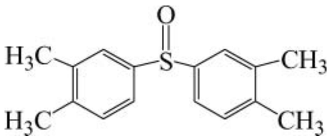
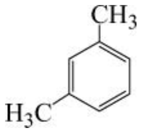
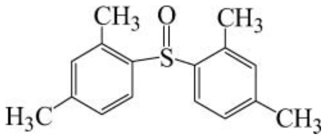
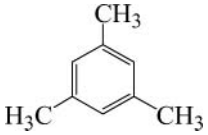
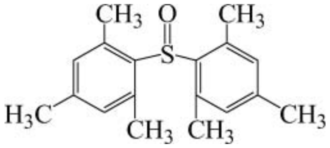
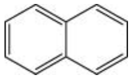
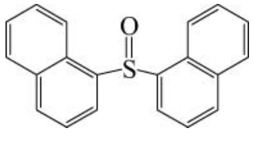
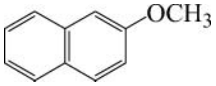
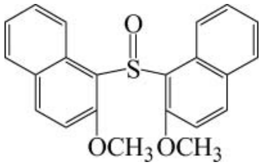


Scheme 1

RESULTS AND DISCUSSION

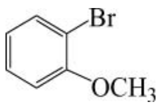
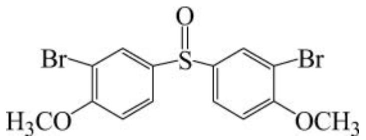
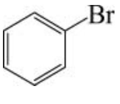
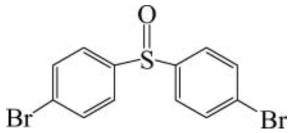
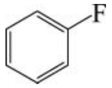
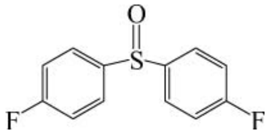
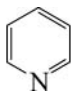
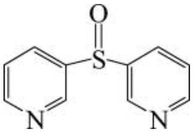
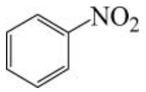
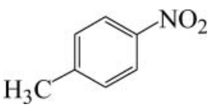
Ps-$AlCl_3$ was prepared by the addition of $AlCl_3$ to polystyrene (8% divinylbenzene) in carbon disulfide under reflux conditions. SiO_2-$AlCl_3$ was prepared by treating silica gel with $AlCl_3$ in refluxing carbon tetrachloride. Sulfinylation of different kinds of arenes with thionyl chloride in the presence of these catalysts was carried out at room temperature in CH_2Cl_2, which proved to be the solvent of choice among other organic solvents (Table I). The optimum molar ratio of Ps-$AlCl_3$ to arene was 0.15:2 and for SiO_2-$AlCl_3$ was 0.1:2. It was observed that both activated and weakly deactivated arenes gave the corresponding sulfoxides in high to excellent yields (Table I, entries 1–12). It is worth noting that acid-sensitive substrate pyridine was converted into the corresponding sulfoxide in excellent yield (entry 13). However, highly deactivated arenes failed to give sulfoxide under the same conditions (entries 14 and 15). The methodology showed the excellent positional selectivity, as the *para* substituted product was formed exclusively. It is probable that mild catalytic activity and steric crowding of the supported catalysts influence higher *para* selectivities observed in the sulfinylation reactions. Side product formation was not observed in the reactions we have studied. Ps-$AlCl_3$ and SiO_2-$AlCl_3$ are stable under the reaction

Table I Sulfinylation of arenes using $SOCl_2$ catalyzed by Ps-$AlCl_3$ and SiO_2-$AlCl_3$[a]

Entry	Arene	Product	Time (h)	Yield (%)[b]
1			1.5^1 1.4^2	$90^{11,28}$ $91^{11,28}$
2			1.4^1 1.3^2	93^{16} 93^{16}
3			1.3^1 1.2^2	92^{20} 93^{20}
4			1^1 0.8^2	93^{18} 92^{18}
5			1.2^1 1.2^2	91^{18} 91^{18}
6			1.2^1 1.1^2	93^{16} 92^{16}
7			1.2^1 1.2^2	92^{16} 92^{16}
8			2.5^1 2.3^2	$87^{18,29}$ $89^{18,29}$
9			2.2^1 2.1^2	90^{18} 90^{18}

(Continued on next page)

Table I Sulfinylation of arenes using $SOCl_2$ catalyzed by Ps-$AlCl_3$ and SiO_2-$AlCl_3$[a] *(Continued)*

Entry	Arene	Product	Time (h)	Yield (%)[b]
10			1.6^{1} 1.5^{2}	91^{18} 92^{18}
11			3^{1} 2.9^{2}	90^{30} 92^{30}
12			3^{1} 3^{2}	88^{16} 90^{16}
13			1.4^{1} 1.2^{2}	92^{31} 92^{31}
14		No reaction	10^{1} 10^{2}	– –
15		No reaction	10^{1} 10^{2}	– –

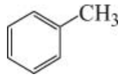
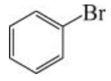
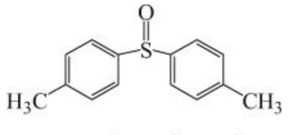
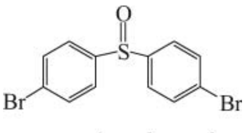
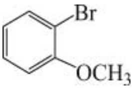
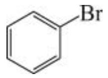
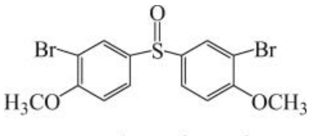
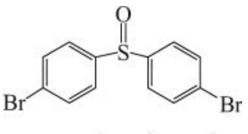
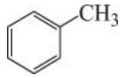
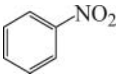
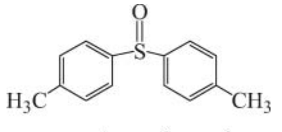
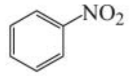
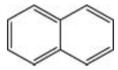
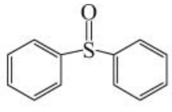
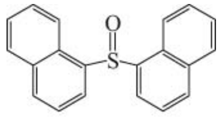
[a] The molar ratio of the arene: $SOCl_2$:Ps-$AlCl_3$^{1} is 2:1.2:0.15 and for SiO_2-$AlCl_3$^{2} is 2:1.2:0.1.
[b] Yields refer to pure isolated products, and all sulfoxides prepared are known compounds and were characterized by comparison of their physical and spectral data with those of the authentic samples.

conditions, and there is no leaching of acid moieties during the reactions. The results show that the order of sulfinylation activity of these catalysts is SiO_2-$AlCl_3$ > Ps-$AlCl_3$.

When Ps-$AlCl_3$ was used as catalyst for sulfinylation, no band corresponding to S=O stretching in the IR spectrum of Ps-$AlCl_3$ was observed after the sulfinylation reaction in either the presence or absence of substrate, indicating that polystyrene itself does not undergo sulfinylation under the experimental conditions used.

To evaluate the selectivity of this method, we investigated competitive reactions for sulfinylation of a variety of arenes using $SOCl_2$ in the presence of Ps-$AlCl_3$, SiO_2-$AlCl_3$, and $AlCl_3$. As shown in Table II, Ps-$AlCl_3$ and SiO_2-$AlCl_3$ are able to discriminate arenes containing electron-donating and electron-withdrawing groups from each other, a transformation that is difficult to accomplish via conventional methods (Table II, entries 1–3). Benzene was selectively converted to the sulfoxide in the presence of naphthalene (entry 4). From the results, it is clear that Ps-$AlCl_3$ and SiO_2-$AlCl_3$ are superior to $AlCl_3$ from the view of higher chemoselectivity and efficiency in sulfinylation reactions. We also observed that the $AlCl_3$-catalyzed reaction produces the corresponding sulfonium salt as a byproduct

Table II Competitive sulfoxide formation reactions using $SOCl_2$ in the presence of Ps-$AlCl_3$, SiO_2-$AlCl_3$, and $AlCl_3$^{a,b}

Entry	Sub. 1	Sub. 2	Prod. 1 (Yield)^{c}	Prod. 2 (Yield (%))^{c}	Time (h)
1			 (93%^{1}, 95%^{2}, 70%^{3})	 (4%^{1} ,4%^{2}, 20%^{3})	1.5
2			 (92%^{1}, 92%^{2}, 68%^{3})	 (5%^{1}, 5%^{2}, 20%^{3})	1.7
3			 (93%^{1}, 95%^{2}, 70%^{3})	 (100%^{1}, 100%^{2}, 100%^{3})	1.5
4			 (91%^{1}, 91%^{2}, 70%^{3})	 (4%^{1}, 4%^{2}, 19^{3})	1.6

^{a}The molar ratio of Subs. 1:Subs. 2:$SOCl_2$ is 2:2:1.1.

^{b}All reactions were carried out in CH_2Cl_2 at room temperature in the presence of Ps-$AlCl_3$ (0.15 mmol),^{1} SiO_2-$AlCl_3$ (0.1 mmol),^{2} and $AlCl_3$ (0.32 mmol).^{3}

^{c}GC yield.

in addition to the sulfoxide.[14] Moreover, $AlCl_3$ might be required for use in reagent quantities due to its complexation of product molecules. The higher chemoselectivity of Ps-$AlCl_3$ and SiO_2-$AlCl_3$ over $AlCl_3$ may be attributed to the mild catalytic activity of these solid catalysts. To the best of our knowledge, these chemoselectivities are new and have not been reported in the literature.

A comparison of the efficiency of Ps-$AlCl_3$ and SiO_2-$AlCl_3$ catalysts with some of those reported in the literature is given in Table III. As is shown in Table III, in addition to having the general advantages attributed to the solid supported catalysts, Ps-$AlCl_3$ and SiO_2-$AlCl_3$ have a good efficiency compared to other recently reported catalysts.

In conclusion, we have developed the use of Ps-$AlCl_3$ and SiO_2-$AlCl_3$ as inexpensive, easy to handle, noncorrosive, stable (as bench top catalysts), reusable (at least five times with negligible loss in their catalytic activity), and environmentally benign catalysts for the synthesis of diaryl sulfoxides from arenes using $SOCl_2$. High chemoselectivity, mild reaction conditions, easy workup, short reaction times, and high to excellent yields are other obvious advantages of the present method.

Table III Comparison of some of the results obtained using Ps-$AlCl_3$ and SiO_2-$AlCl_3$ with some other catalysts used for direct sulfinylation of arenes with $SOCl_2$

Arene	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)
Anisole	TfOH	Neat	rt	2	95[17]
	$Sc(OTf)_3$	CH_2Cl_2	rt	1.5	90[18]
	$H_3PW_{12}O_{40}$[a]	Neat	rt	2.5	94[20]
	SiO_2-$AlCl_3$	CH_2Cl_2	rt	1.2	93
	Ps-$AlCl_3$	CH_2Cl_2	rt	1.3	92
Benzene	[Bmim]Cl.$AlCl_3$[b]	Neat	rt	5 min	85[19]
	SiO_2-$AlCl_3$	CH_2Cl_2	rt	1.4	91
	Ps-$AlCl_3$	CH_2Cl_2	rt	1.5	90
Toluene	Sulfated zirconia	Neat	rt	1.5	90[21]
	SiO_2-$AlCl_3$	CH_2Cl_2	rt	1.3	93
	Ps-$AlCl_3$	CH_2Cl_2	rt	1.4	93

[a] Tungstophosphoric acid (heteropoly acid).

[b] 1-Butyl-3-methylimidazolium chloroaluminate (ionic liquid).

EXPERIMENTAL

Chemicals were either prepared in our laboratory or were purchased from Merck and Fluka. Polystyrene (8% divinylbenzene, prepared via suspension polymerization, polyvinylpyrrolidone 90 K as suspension agent, grain size range: 0.25–0.6 mm) was obtained from Iran Polymer and Petrochemical Institute. Gas chromatography was recorded on a Shimadzu GC 14-A. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer using $CDCl_3$ as solvent and TMS as the internal standard. Capacities of the catalysts were determined by gravimetric method and atomic absorption technique using a Philips atomic absorption instrument. Melting points were determined on a Fisher-Jones melting-point apparatus and are uncorrected. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica-gel polygram SILG/UV_{254} plates.

Preparation of Ps-$AlCl_3$ and SiO_2-$AlCl_3$

These catalysts were prepared as reported in the literature.[27] The capacities of Ps-$AlCl_3$ and SiO_2-$AlCl_3$ obtained by gravimetric method and checked by atomic absorption technique were 0.4 and 1.3 mmol $AlCl_3$ per gram, respectively.

Typical Procedure for Sulfinylation of Anisole with $SOCl_2$

To a solution of anisole (2 mmol) and Ps-$AlCl_3$ (0.15 mmol) or SiO_2-$AlCl_3$ (0.1 mmol) in CH_2Cl_2 (10 mL), $SOCl_2$ (1.2 mmol) was added dropwise, and the resulting mixture was stirred at ambient temperature under N_2 atmosphere. Progress of the reaction was monitored by TLC and GC. After completion of the reaction, the catalyst was filtered off and washed with CH_2Cl_2 (2 × 10 mL). The filtrate was then treated with saturated sodium bicarbonate (15 mL), extracted with CH_2Cl_2 (2 × 10 mL), and dried over anhydrous Na_2SO_4. Evaporation of the solvent on a rotary evaporator under reduced pressure gave di-(4-methoxyphenyl) sulfoxide.[20] Whenever required, the products were purified by column chromatography so as to afford the pure diaryl sulfoxide. The spent catalyst from different experiments was washed with ether and used again without further drying.

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