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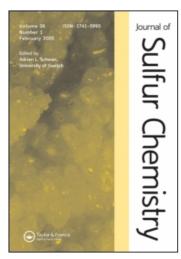
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Kaveh Parvanak Boroujeni^a

^a Department of Chemistry, Shahrekord University, Shahrekord, Iran

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Sulfonylation of aromatic compounds with sulfonic acids using silica gel-supported AlCl₃ as a heterogeneous Lewis acid catalyst

Kaveh Parvanak Boroujeni*

Department of Chemistry, Shahrekord University, Shahrekord 115, Iran

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Silica gel-supported aluminum chloride (SiO₂–AlCl₃) has been shown to be a mild, efficient, and chemoselective heterogeneous Lewis acid catalyst for direct conversion of arenes to sulfones using sulfonic acids as sulfonylating agents. The catalyst can be prepared easily with cheap starting materials and is stable (as a bench-top catalyst) and reusable.

Keywords: sulfonylation; sulfones; sulfonic acids; aluminum chloride; silica gel

1. Introduction

In recent years, the use of solid-supported catalysts has received considerable attention in different areas of organic synthesis (1). The activity and selectivity of a catalyst dispersed on the surface of a support is improved as the effective surface area of the catalyst is increased manifold, and hence they are expected to perform more effectively than the individual catalysts. Recyclability, easily separable from the reaction media, moisture and air tolerance, non-toxicity, and easier handling are other common features that make the use of solid-supported catalysts an attractive alternative to conventional homogeneous catalysts (2).

Organosulfones are useful intermediates in a wide range of fields such as agrochemicals (3), pharmaceuticals (4, 5), and polymers (6). In particular, aryl sulfones have received much attention as powerful anti-HIV-1 agents (7). They also possess high antifungal, antibacterial, and antitumoral activities (8, 9). The most practical laboratory method of preparing aryl sulfones is Friedel–Crafts sulfonylation of arenes (10, 11). Typically, sulfonyl chlorides are used as the sulfonylating agents and stoichiometric or excess amounts of Lewis acids such as AlCl₃ and SbF₅ are required (12–22). This procedure has serious drawbacks since sulfonyl chlorides and metallic oxophilic promoters cause environmental problems due to strongly acidic waste streams. Further, tedious work-up, highly corrosive conditions, the formation of various side products, and the use of moisture-sensitive, unrecyclable, or difficult to handle catalysts are other disadvantages of the classical method. These disadvantages could be avoided by performing the sulfonylation of arenes

*Email: parvanak-ka@sci.sku.ac.ir

$$\begin{array}{c|c} & & ArSO_3H \\ \hline \\ SiO_2-AlCl_3 \\ \hline \\ Y \\ \end{array} \begin{array}{c} Ar - O \\ SiO_2-AlCl_3 \\ \hline \\ O \\ Y \\ \end{array} \begin{array}{c} Ar: ph, tolyl \\ Y: H, OMe, Me, \\ ph, Cl, Br \\ \end{array}$$

Scheme 1. Sulfonylation of arenes with sulfonic acids using SiO₂–AlCl₃.

with sulfonic acids as sulfonylating agents over recoverable solid acid catalysts. Sulfonic acids are probably the best sulfonylating reagents since they are common precursors of sulfonyl chlorides and their reactions produce water as the only by-product, which meets the recent requirement for environmentally benign processes. In addition, in this method the products are purer than those obtained by the Friedel-Crafts method and the isolation of products is simple with no need of acid removal. Sulfonylation involving sulfonic acids has been studied, although these procedures are not quite successful as practical and general synthetic methods (23–31). For instance, Graybill reported polyphosphoric acid as a catalyst for the direct sulfonylation of arenes (23). However, polyphosphoric acid is a viscous liquid and is not easy to handle, and the reaction suffers from low yields and long reaction times. MeSO₃H/P₂O₅ (as a dehydrating agent) has been studied for the synthesis of sulfones using sulfonic acids (26). This method has certain disadvantages such as being time-consuming, the thermal decomposition of the reagent, and using a 10-fold excess of methane-sulfonic acid. Recently, it was also shown that Fe³⁺-montmorillonite, Nafion-H, and P₂O₅/Al₂O₃ promote the sulfonylation of arenes using sulfonic acids (13, 27, 30). Although these methods are environmentally safe, the reactions have some limitations such as unsatisfactory yields, long reaction times, and reflux conditions. Sulfonylation of arenes using sulfonic acids without the need of any catalyst has been reported but in this method the reactions occur in the presence of 1.5 molar equivalents of Tf₂O in CH₃NO₂ which results in a substantial amount of waste and in corrosion problems (31). In view of this, a reliable method for this useful reaction involving heterogeneous catalysts is in demand.

In a continuation of recent work on the use of heterogeneous Lewis acid catalysts, a report has been published on silica gel-supported aluminum chloride (SiO_2 -AlCl₃) as an effective catalyst for the sulfonylation of aromatic compounds with sulfonyl chlorides (32). Along this line, I further wish to report that SiO_2 -AlCl₃ (33–35) is also a highly efficient and chemoselective catalyst for the sulfonylation of arenes using p-toluenesulfonic acid (TsOH) and benzene sulfonic acid (PhSO₃H) in solvent-free conditions (Scheme 1).

2. Results and discussion

 SiO_2 –AlCl₃ was prepared by treating silica gel with AlCl₃ in refluxing carbon tetrachloride. As shown in Table 1, different kinds of aromatic compounds underwent sulfonylation with PhSO₃H and TsOH as sulfonylating agents effectively to afford sulfones at 80 °C. It was observed that the electron donating groups such as alkyl and OMe on the aromatic compound gave high to excellent yields of the product (Entries 2–7). Also, weakly deactivated arenes such as chlorobenzene and bromobenzene underwent sulfonylation with high yields (Entries 8–9). However, sulfonylation of highly deactivated arenes such as nitrobenzene and 1,2-dichlorobenzene failed. The methodology showed excellent positional selectivity as the *para*-substituted product was formed exclusively. Naphthalene was converted to the corresponding sulfones with high regioselectivity in high yields (Entry 10). The sulfonylation of indole with sulfonic acids in the presence of SiO_2 –AlCl₃ was also studied and the corresponding 3-arylsulfonyl indoles were obtained in 90–92% yields (Entry 11). No N-substituted products were observed under these reaction conditions. The optimum molar

Table 1. Sulfonylation of arenes with sulfonic acids using SiO_2 -AlCl $_3$.

Entry	Arene	Ar	Product	Time (h)	Yield (%) (o:m:p) ^b	m.p. (°C) (reported)	Ref.
1	Benzene	Ph	SO ₂ C ₆ H ₅	1.5	90	125–127 (123)	(23)
		Tolyl	$SO_2C_6H_4Me-4$	1.5	90	128 (125)	(23)
2	Toluene	Ph	SO ₂ C ₆ H ₅ Me	1.4	91 (6:4:90)	79–80 (78–79)	(14)
		Tolyl	SO ₂ C ₆ H ₄ Me-4 Me	1.4	92 (6:4:90)	147–150 (146–149)	(14)
3	Biphenyl	Ph	SO ₂ C ₆ H ₅	1.5	90 (6:0:94) ^c	147–150 (148)	(23)
		Tolyl	$SO_2C_6H_4Me-4$ Ph	1.5	91 (5:0:95) ^c	173–175 (178)	(23)
4	o-Xylene	Ph	SO ₂ C ₆ H ₅ Me Me	1.5	91 (93:7) ^d	88–90 (86–88)	(14)
		Tolyl	$Me \bigvee_{Me}^{SO_2C_6H_4Me-4}$	1.4	92 (92:8) ^d	117–119 (113–115)	(14)
5	m-Xylene	Ph	Me $SO_2C_6H_5$	1.5	91	91–94 (92–94)	(14)
		Tolyl	Me Me $SO_2C_6H_4Me-4$	1.4	93	50–52 (49)	(26)
6	p-Xylene	Ph	$\operatorname{SO_2C_6H_5}_{\operatorname{Me}}$	1.5	92	103–105 (101–103)	(14)
		Tolyl	$\begin{tabular}{ll} Me \\ SO_2C_6H_4Me-4 \\ Me \end{tabular}$	1.5	93	107–109 (104)	(13)

Table 1. Continued.

Entry	Arene	Ar	Product	Time (h)	Yield (%) (o:m:p) ^b	m.p. (°C) (reported)	Ref.
7	Anisole	Ph	SO ₂ C ₆ H ₅	1.3	93 (8:3:89)	76–78 (79–80)	(14)
		Tolyl	SO ₂ C ₆ H ₄ Me-4 OMe	1.3	94 (7:3:90)	101–104 (104)	(26)
8	Chlorobenzene	Ph	SO ₂ C ₆ H ₅	1.9	88 (9:5:86)	79–81 (77–78)	(14)
		Tolyl	$SO_2C_6H_4Me-4$	1.9	88 (8:3:89)	118–120 (123)	(26)
9	Bromobenzene	Ph	SO ₂ C ₆ H ₅	1.8	89 (6:3:91)	91–94 (92–94)	(14)
		Tolyl	SO ₂ C ₆ H ₄ Me-4 Br	1.8	90 (4:5:91)	133–135 (136–137)	(15)
10	Naphthalene	Ph	SO ₂ C ₆ H ₅	2.6	85 (10:90) ^e	70–73 (69–71)	(14)
		Tolyl	SO ₂ C ₆ H ₄ Me-4	2.7	90 (9:91) ^e	103–106 (102–104)	(14)
11	Indole	Ph	$\bigotimes_{\substack{N\\I\\H}}^{SO_2C_6H_5}$	2.3	90°	145–147 (147)	(36)
		Tolyl	$\underbrace{ \begin{array}{c} \mathrm{SO_2C_6H_4Me\text{-}4} \\ N \\ I \\ H \end{array} }$	2.3	92 ^c	173–176 (172–173)	(37)

Notes: a All reactions were carried out at 80 o C in the presence of SiO₂–AlCl₃. The molar ratio of the sulfonic acid: SiO₂–AlCl₃ is: 1:0.1. b Yield refers to the mixture of isomeric products. Isomer distribution based on 1 H NMR study of crude sulfones. o The reaction was performed in acetonitrile. d Isomer distribution of 3,4-dimethylphenyl isomer to 2,3-dimethylphenyl isomer. o α : β ratio. The reaction was performed in acetonitrile.

Note: aRecovered catalyst was used successively (Use 2,3,...).

Scheme 2. Sulfonylation of toluene using recovered SiO₂–AlCl₃.

ratio of SiO₂-AlCl₃ to sulfonylating agent was 0.1:1. Side product formation was not observed in the reactions we have studied.

In order to show the role of the silica gel in the sulfonylation reactions, we performed sulfonylation of anisole with TsOH in the presence of AlCl₃ (1.5 equiv.) at 80 °C in the absence of silica gel. We have observed that the corresponding sulfone was produced with 40% yield after 3.5 h, whereas the desired sulfone was isolated with 94% yield after 1.3 h in the presence of SiO₂–AlCl₃ (Table 1, Entry 7). Presumably, the lower catalytic activity of AlCl₃ than SiO₂–AlCl₃ in sulfonylation of arenes with sulfonic acids is due to its ability to strongly complex Lewis base products. Unlike AlCl₃, SiO₂-AlCl₃ is a milder catalyst which forms no stable complex with starting materials and/or products. Further, the presence of silica makes the present method even more effective, as it acts as a water scavenger. It should be noted that in the absence of silica, the reaction required forcing conditions, azeotropic removal of water using a Dean-Stark trap (13, 27).

To find out whether the reaction takes place in the solid matrix of SiO₂-AlCl₃ or whether AlCl₃ simply released in the reaction medium is responsible for the sulfonylation reaction, SiO₂– AlCl₃ was added to anisole and the mixture was stirred at room temperature for 2 h. Then, the catalyst was filtered off and the filtrate was analyzed for its aluminum content, which showed a negligible release of AlCl₃. The filtrate was found to be inactive for the sulfonylation reaction. These observations indicate that SiO₂-AlCl₃ is stable under the reaction conditions and there is no leaching of acid moieties during reactions due to being chemically bonded to the support.

The recyclability of the catalyst was also studied. The spent catalyst from sulfonylation reactions was washed with ether and used again without further drying. The activity of the catalyst was unaffected even after five cycles (Scheme 2). The capacity of the catalyst after five uses was 1.3 mmol AlCl₃ per gram.

Experimental

General 3.1.

Chemicals were either prepared in our laboratory or were purchased from Merck and Fluka. The capacity of the catalyst was determined by the Mohr titration method and atomic absorption technique using a Philips atomic absorption instrument. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica gel polygram SILG/UV₂₅₄ plates. Gas chromatographic analysis was performed on Shimadzu GC. 14-A. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Advance DPX-300 spectrometer.

3.2. Preparation of $SiO_2 - AlCl_3$ (32, 38)

Anhydrous AlCl₃ (5.1 g) was added to silica gel (Merck grade 60, 230–400, washed with 1 M HCl and dried under vacuum at 80 °C for 72 h, 10.2 g) in carbon tetrachloride (30 ml). The mixture was stirred using a magnetic stirrer under reflux condition for 2 days under N₂ atmosphere and filtered and washed with 50 ml of dry CCl₄, and then dried under vacuum at 60 °C for 3 h. The loading of AlCl₃ determined was 1.3 mmol/g. (One gram of solid catalyst was fused with Na metal, extracted with 10 ml of water and filtered. The aluminum and chloride content of the filtrate was determined by the Mohr titration method [for the procedure refer to (39)]).

3.3. Typical experimental procedure

In a round-bottomed flask (25 ml) equipped with a condenser and a magnetic stirrer, a solution of m-xylene (10 mmol) and TsOH (7.5 mmol) was prepared. SiO₂-AlCl₃ (0.75 mmol) was added to the solution and the reaction mixture was stirred magnetically at 80 °C. Progress of the reaction was followed by TLC and GC. After completion of the reaction, the catalyst was filtered off and washed with CH₂Cl₂ or ether (2 × 15 ml) and the filtrate was washed with 10% NaHCO₃ solution (2 × 10 ml) and water (10 ml). The combined organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuo, and the residue was recrystallized from CH₂Cl₂/n-hexane to give (2,4-dimethylphenyl)tolylsulfone as a white crystalline solid, yield 93%. All products are known compounds and were identified by comparing their physical and spectral data with those of the authentic samples (13, 14, 25). Representative examples of spectroscopic data are given below.

Di(*p*-tolyl) sulfones (Table 1, Entry 2): ¹H NMR (300 MHz; CDCl₃) δ 2.30 (s, 5.40H, *para* isomer), 2.36 (s, 0.24H, *meta* isomer), 2.41 (s, 0.36H, *ortho* isomer), 7.26 (d, J = 8.0 Hz, 4H), 7.79 (d, J = 8.0 Hz, 4H); IR (KBr) 1160, 1315 cm⁻¹.

(2,4-Dimethylphenyl)p-tolylsulfone (Table 1, Entry 5): 1 H NMR (300 MHz; CDCl $_3$) δ 2.40 (s, 3H), 2.41 (s, 3H), 2.45 (s, 3H), 7.12 (s, 1H), 7.24 (d, 1H), 7.80 (2H, d), 7.78 (2H, d), 8.09 (d, 1H); IR (KBr) 1157, 1315 cm $^{-1}$.

Napthyltolylsulfone (Table 1, Entry 10): ¹H NMR (300 MHz; CDCl₃) δ 2.26 (s, 2.73H, β -isomer), 2.28 (s, 0.27H, α -isomer), 7.28 (m, 2H), 7.5–7.64 (m, 2H), 7.80–8.16 (m, 5H), 8.55 (d, J = 8.6 Hz, 1H), 8.71 (d, J = 8.5 Hz, 1H).

3-(4-Methylphenylsulfonyl)-1*H*-indole (Table 1, Entry 11): 1H NMR (300 MHz, CDCl₃): δ 2.25 (s, 3H), 6.81–6.90 (m, 4H), 7.07–7.19 (m, 2H), 7.27–7.31 (m, 2H), 7.49 (d, 1H, J=8.0 Hz), 8.19 (brs, NH); IR (KBr) 3330, 1582, 1450, 1388, 1299, 1230, 1147, 1097, 758 cm⁻¹.

4. Conclusion

In summary, SiO₂–AlCl₃ is an effective and chemoselective heterogeneous Lewis acid catalyst for the direct sulfonylation of arenes using sulfonic acids, with possible application in "green chemistry" scenarios by virtue of its activity under solventless conditions and its ability to be recycled. Mild reaction conditions, easy workup, short reaction times, and high to excellent yields are other obvious advantages of the present method.

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