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A novel method for sulfonation of aromatic rings with silica sulfuric acid

Abdol R. Hajipour,[a,b,*] Bi Bi F. Mirjalili,[c] Amin Zarei,[a] Leila Khazdooz[c] and A. E. Ruoho[b]

[a] *Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran*
[b] *Department of Pharmacology, University of Wisconsin Medical School, 1300 University Avenue, Madison, WI 53706-1532, USA*
[c] *Department of Chemistry, College of Science, Yazd University, Yazd, Iran*

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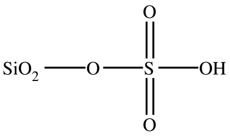
Abstract—Direct and chemoselective sulfonation of aromatic compounds with silica sulfuric acid in 1,2-dichloeoethane or under solvent-free conditions.

The sulfonation of aromatic compounds are very important and many aromatic hydrocarbons have been sulfonated.[1,2] The common methods for synthesis of sulfonic acids are employing oxidation of a thiol or a thioether with ether,[3] sulfonation of Grignard and lithium reagents,[4] nucleophilic aromatic substitution with sodium sulfite,[5] sulfonation of aromatic compounds with concentrated sulfuric acid,[6] sulfonation with sulfur trioxide–dioxane complex,[7] trifluro acetic acid–sulfuric acid,[8] and sulfur trioxide in dichloromethane.[9]

In continuation of our studies on the application of solid acids we found that silica gel reacts with chlorosulfonic acid to give silica sulfuric acid (I). It is interesting to note that the reaction is easy, clean and without any needed work-up procedure because HCl gas is evolved from the reaction vessel immediately. We also found that silica sulfuric acid (I) is an excellent candidate for sulfuric acid replacement in organic reactions without any limitations such as destruction of acid sensitive functional groups.[10] To determine the stability of this reagent, we kept 1 g of the reagent at 200 °C for 8 h and discovered that the reagent did not lose any weight or activity.



$$SiO_2-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

I

We wish here to report a mild and efficient method for synthesis of arylsulfonic acids with silica sulfuric acid for conversion of a variety of aromatic compounds in 1,2-dichloroethane or in excess of substrate without using any solvent to the corresponding sulfonic acids (Scheme 1). In sulfonation of aromatic compounds, the sulfonic acids are often in equilibrium with sulfones as a byproducts. However, at lower temperatures the equilibrium is very slow and is favorable for the formation of corresponding sulfonic acids.[11] In this method since silica sulfuric acid is used for sulfonation at moderate temperature and also as silica sulfuric acid is bulky, therefore this reagent reacts with high selectivity and the reverse reaction is low and the sulfones are not produced at all. We tried the reaction of silica sulfuric acid in excess of a variety of aromatic compounds without using any solvent at 80 °C (Table 1). In comparison to reaction in 1,2-dichloroethane at 80 °C, the yield of the reaction in excess of substrate is higher; this may be due to the high concentration of substrate in the later method. Another noteworthy point of this

$$ArH + SIO_2O\text{-}SO_3H \xrightarrow[30\ \text{min}]{80\ ^{\circ}C} ArSO_3H + SIO_2\text{-}OH$$

Scheme 1.

Keywords: Sulfonation; Silica sulfuric acid; Aromatic compound; Sulfonic acid.

[*] Corresponding author. Tel.: +98-113913262; fax: +98-112350; e-mail: haji@cc.iut.ac.ir

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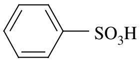
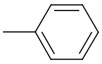
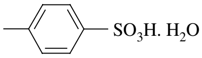
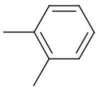
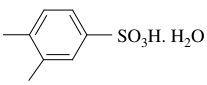
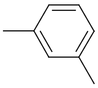
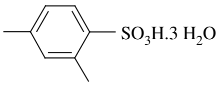
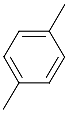
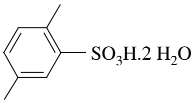
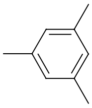
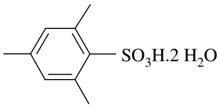
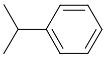
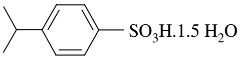
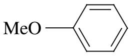
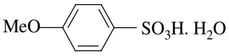
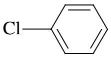
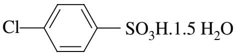
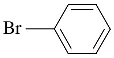
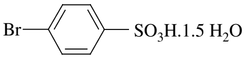
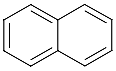
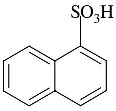
Table 1. Sulfonation of aromatic compound with silica sulfuric acid in 1,2-dichloroethane and in excess of substrate at 80 °C[12,13]

Entry	Substrate	Product	Yield (O:M:P) % in 1,2-dichloroethane	Yield (O:M:P) % in excess of substrate	Melting point (°C)
1			40	80	45–49
2			45 (10:0:90)	85 (10:0:90)	99–103
3			46	80	80–84
4			43	85	62–65
5			47	85	88–90
6			40	75	74–76
7			37 (0:0:100)	65 (0:0:100)	—
8			56 (0:0:100)	90 (0:0:100)	86–88
9			48 (0:0:100)	85 (0:0:100)	85–87
10			46 (0:0:100)	80 (0:0:100)	103–105
11			60	45[a]	78–80

[a] Reaction condition: 0.38 g (1 mmol) silica sulfuric acid and 0.12 g (1 mmol) naphthalene were ground and placed in oven at 80 °C for 30 min.

method is that the reaction proceeds under heterogeneous conditions and also the silica gel can be used several times without losing its activity.

The advantage of this methodology is the availability of the starting materials, simplicity of sulfonation procedure under heterogeneous system, clean, and straightforward work-up, short reaction time, high yields without formation of sulfones as by-products.

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12. Typical procedure for preparation of sulfonic acids in excess of substrate: Preparation of mesitylene sulfonic acid: A 25 mL round bottomed flask was charged with silica sulfuric acid[10] (1.9 g, 5 mmol) and mesitylene (5 mL) and a magnetic stirrer. The reaction mixture was stirred at 80 °C for 30 min, the heterogeneous mixture then was filtered, washed with 10 mL of dichloromethane, and the solvent was removed under reduced pressure. The residue

was washed with *n*-hexane (2 × 10 mL) and dried in air to produce white solid (0.75 g, 75% yield), mp: 74–76 °C (reported: 76–78 °C),[14] ^{1}H NMR δ (90 MHz, DMSO) 7.8 (S, 5H, OH, $2H_2O$), 6.7 (S, 2H), 2.6 (S, 6H), 2.2 (S, 3H), IR (KBr) cm^{-1}: 2700–3500 (br, SO_3H), 1120–1230 (S).

13. Typical procedure for preparation of sulfonic acids in 1,2-dicholoroethane: Preparation of mesitylene sulfonic acid: A 25 mL round bottomed flask was charged with silica sulfuric acid[10] (0.38 g, 1 mmol), mesitylene (0.13 mL, 1 mmol), and 1,2-dichloroethane (5 mL) and a magnetic stirrer. The reaction mixture was stirred at 80 °C for 30 min, the heterogeneous mixture then was filtered, washed with 10 mL of dichloromethane, and the solvent was removed under reduced pressure. The residue was washed with *n*-hexane (2 × 10 mL) and dried in air to produce white solid (0.08 g, 40% yield).
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