Communication

Aluminium Nitrate/Silica Sulfuric Acid/Bromide Ion: As an Effective and Catalytic Oxidizing Media for the Selective Oxidation of Sulfides to Sulfoxides

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Various types of sulfides are chemoselectively oxidized to the corresponding sulfoxides by treatment of $Al(NO_3)_3.9H_2O$, silica sulfuric acid and a catalytic amount of NaBr in the presence of wet SiO_2 (50% *w/w*) in CH_2Cl_2 at room temperature. The catalytic oxidation procedure is very simple and the products are easily isolated in good yields.

Keywords: Sulfides; Sulfoxides; Homoselectivity; Aluminium nitrate; Silica sulfuric acid.

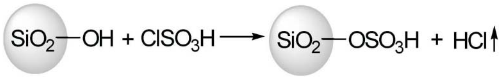
The design and development of heterogeneous catalysts are one of the most important objectives in the current area of research interest. The Important aspect of clean technology is the use of environmentally friendly catalysts.[1] Recently, the development of efficient and new catalytic systems for various organic transformations is an active ongoing research area and the scope for further improvement towards milder reaction conditions.[2]

The chemistry of sulfoxides has been attractive to organic chemists. Because sulfoxides are valuable synthetic intermediates for the construction of chemically and biologically important significant molecules.[3-5] Sulfoxides have also been used extensively in organic synthesis such as C-C bond-forming, molecular rearrangements and functional group transformations.[6-10] Although various oxidizing agents are used for this purpose,[11-32] unfortunately, some of these reagents are not satisfactory for the selective oxidation of sulfides to the sulfoxides because of several reasons. The first reason is that sulfoxides can undergo overoxidation to sulfones and therefore it is important that the catalyst has low reactivity towards the sulfoxides. Other serious obstacles of the previous procedures are long reaction time, low selectivity, low yields of products, toxicity, and expensive reagents.

In continuation of our recent studies on the oxidation reactions,[33-39] we have been enthusiastic to introduce a new catalytic media, based on in situ generation of X^+ using aluminium nitrate $\{Al(NO_3)_3.9H_2O\}$, silica sulfuric acid $\{SiO_2\text{-}OSO_3H\}$ and a metal halide.

Silica sulfuric acid can be easily prepared by the reaction of chlorosulfonic acid with silica gel (Scheme I).[40]

Scheme I



To find the best reaction conditions for the oxidation of sulfides, a combination of $Al(NO_3)_3.9H_2O$, silica sulfuric acid and catalytic amounts of a metal halide (MX) in the presence of wet SiO_2 (50% *w/w*) in dichloromethane at room temperature was examined for the oxidation of benzyl phenyl sulfide as a model reaction, and the results are summarized in Table 1. As can be seen from Table 1, the best result is referred to $Al(NO_3)_3.9H_2O$, silica sulfuric acid and wet SiO_2 (50% *w/w*) in the presence of catalytic amount of NaBr.

Consequently, we presented a new heterogeneous catalytic protocol for the selective oxidation of different types of sulfides **1** to the corresponding sulfoxides **2** using combination of $Al(NO_3)_3.9H_2O$ **I**, silica sulfuric acid **II** and wet SiO_2 (50% *w/w*) in the presence of catalytic amounts of NaBr **IV** in dichloromethane at room temperature in excellent yields (Scheme II and Table 2).

To show the role of bromide ion as a catalyst in the described system benzyl phenyl sulfide was subjected to the

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Table 1. Oxidation of benzyl phenyl sulfide by $Al(NO_3)_3.9H_2O$ **I**, silica sulfuric acid **II** and catalytic amounts of a metal halide (MX) **III** in the presence of wet SiO_2 (50% *w/w*)[a] in CH_2Cl_2 at room temperature

Entry	Catalyst	Substrate/Reagents/Catalyst[b]			Time (Min)	Yield (%)[c]
		I	**II**	**III**		
1	NaCl	1.2	0.2	0.05	240	---[d]
2	NaBr	1.2	0.2	0.05	45	98
3	NaI	1.2	0.2	0.05	240	---[d]
4	KBr	1.2	0.2	0.05	70	92
5	--	1.2	0.2	--	16 h	--[e]
6	NaBr	1.2	--	0.05	7 h	--[d]

[a] substrate : wet SiO_2 = 1 mmol : 0.2 g.

[b] **I** and **III** refer to mmol of $Al(NO_3)_3.9H_2O$ and MX; **II** refers to the gram of the silica sulfuric acid.

[c] Isolated yield.

[d] Reaction didn't complete.

[e] Reaction didn't complete and impurity of sulfone was observed.

oxidation reaction without NaBr, however, the reaction did not complete after 16 hours and impurity of sulfone was observed on the TLC (Table 2, entry 3).

Also, in Table 2, entry 4, which is shown that the sulfoxidation reaction did not complete in the absence of silica sulfuric acid as source of proton; which means acidic media is necessary for this transformation by described catalytic system.

Additionally, this oxidizing catalytic media allowed the homoselective,[39] oxidation of thiantrene to thianthrene monosulfoxide (Table 2, entry 9, Scheme III).

To show the chemoselectivity of the described system, a sulfide including hydroxyl group were subjected to the sulfoxidation reaction, but alcohol oxidation did not occur under the above-mentioned conditions, and primary hydroxyl group remained intact in the course of the reaction (Table 2, entry 7, Scheme IV).

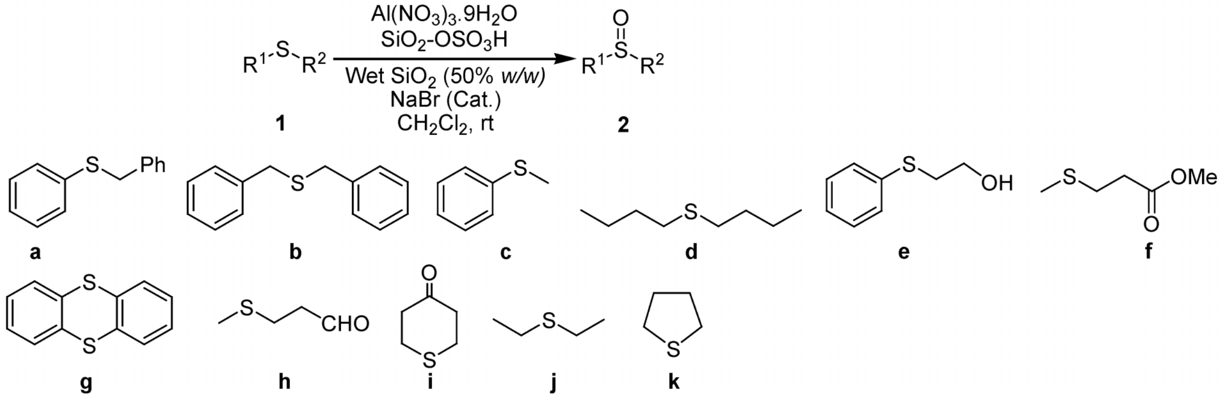
A plausible mechanism of this oxidation is shown in Scheme V based on reported pathway in literatures,[35,39] our observations, and the obtained results.

In summary, we report an efficient method for the selective oxidation of sulfides to sulfoxides under mild and heterogeneous conditions with good to high yields. In addition, chemoselectivity, the cheapness and availability of the reagents and catalyst, easy and clean work-up and high yields make this method attractive for chemists.

EXPERIMENTAL

The chemicals and solvents were supplied by Fluka, Merck and Aldrich chemical companies without further

Scheme II



Scheme III

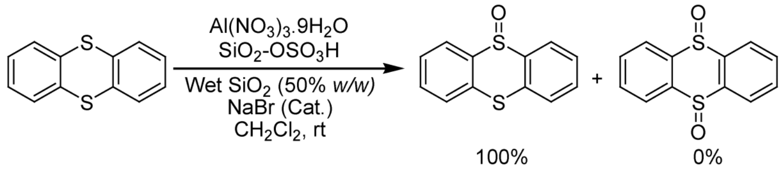


Table 2. Oxidation of sulfides **1** to the corresponding sulfoxides **2** using combination of $Al(NO_3)_3.9H_2O$ **I**, silica sulfuric acid **II** and wet SiO_2 (50% *w/w*)[a] in the presence of catalytic amounts of NaBr **IV** in dichloromethane at room temperature

Entry	Substrate	Product	Substrate/Reagent/Catalyst[b]			Time (Min)	Yield (%)[c]	Ref.[d]
			I	**II**	**IV**			
1	**1a**	**2a**	1.2	0.2	0.05	45	98	12, 14, 15, 39-42
2	**1a**	**2a**	1.2	0.2	--	16 h	--[e]	--[e]
3	**1a**	**2a**	1.2	--	0.05	7 h	--[f]	--[f]
4	**1b**	**2b**	1.2	0.2	0.05	35	97	12, 15, 39-42
5	**1c**	**2c**	1.2	0.2	0.05	20	96	14, 15, 39-42
6	**1d**	**2d**	1.2	0.2	0.05	20	98	12, 15, 39-42
7	**1e**	**2e**	1.2	0.2	0.05	3.5 h	99	15, 39
8	**1f**	**2f**	1.2	0.2	0.05	30	98	39
9	**1g**	**2g**	1.2	0.2	0.05	40	99	39, 41
10	**1h**	**2h**	1.2	0.2	0.05	15	19	15, 39
11	**1i**	**2i**	1.2	0.2	0.05	25	92	41
12	**1j**	**2j**	1.2	0.2	0.05	20	80	42
13	**1k**	**2k**	1.2	0.2	0.05	20	81	15, 41

[a] substrate : wet SiO_2 = 1 mmol : 0.2 g.

[b] **II** refer to gram of silica sulfuric acid; **I** and **IV** refer to mmol of aluminium nitrate and catalyst.

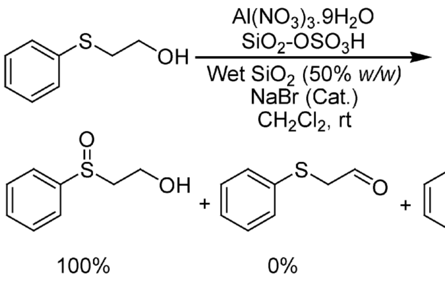
[c] Isolated yield.

[d] All products are known and were identified using comparison of their physical and spectral data (IR, NMR, or MS) with those reported in the literature.

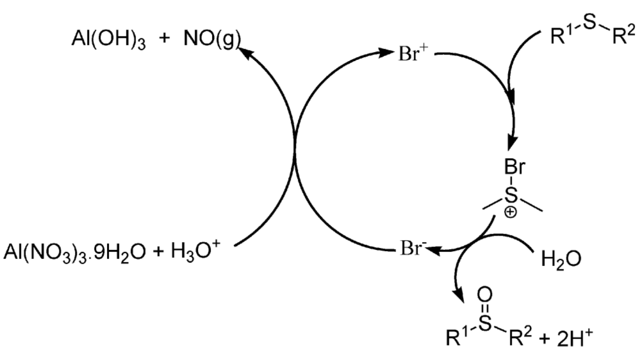
[e] In the absence of catalyst; reaction didn't complete and impurity of sulfone was observed.

[f] In the absence of silica sulfuric acid; reaction didn't complete.

Scheme IV



Scheme V



purifications.

Oxidation of methyl phenyl sulfide 1c to methyl phenyl sulfoxide 2c with $Al(NO_3)_3.9H_2O$, SiO_2-OSO_3H, wet SiO_2 (50% *w/w*) and NaBr

NaBr (0.005 g, 0.05 mmol), $Al(NO_3)_3.9H_2O$ (0.45 g, 1.2 mmol), silica sulfuric acid (0.2 g) and wet SiO_2 (50% *w/w*), (0.2 g) was added to a solution of methyl phenyl sulfide **1c** (0.124 g, 1 mmol) in CH_2Cl_2 (5 mL). The resulting reaction mixture was stirred at room temperature for 20 min (the reaction progress was monitored by TLC) and then filtered. The residue was washed with CH_2Cl_2 (4 × 5 mL). Anhydrous Na_2SO_4 (1.5 g) was added to the filtrate and filtered off after 20 min. Finally CH_2Cl_2 was removed and methyl phenyl sulfoxide **2c** was obtained in 96% yield (0.134 g).

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