

Guanidinium Nitrate/Silica Sulfuric Acid/Ammonium Bromide as an Effective, Viable and Metal-free Catalytic Media for the Selective Oxidation of Sulfides to the Sulfoxides

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In the last few years, heterogeneous systems¹⁻⁴ has become increasingly used in organic synthesis, mainly because the reactions are carried out under mild conditions and the organic products are easily isolated from the reaction media. In addition, the stability and cheapness, high yields of the products, short reaction times, and reusability is other important advantages of these systems.⁵

Chemoselective oxidation of sulfides to sulfoxides is an important synthetic method because corresponding sulfoxides are valuable synthetic intermediates for the synthesis of chemically and biologically significant molecules.⁶⁻⁸ Sulfoxides are also valuable in C-C bond-forming^{9,10} and molecular rearrangements.¹¹⁻¹³ Even though various approaches have been reported for the oxidation of sulfides to sulfoxides such as H₂O₂/iron(III)-salen,¹⁴ *tert*-butyl hydroperoxide/Ti(*i*PrO)₄/1,2-diphenylethane-1,2-diol,¹⁵ TaCl₅/H₂O₂,¹⁶ sodium perborate or sodium percarbonate/silica sulfuric acid/KBr,¹⁷ 3-carboxypyridinium chlorochromate/AlCl₃,¹⁸ ZrCl₄/H₂O₂,¹⁹ ceric ammonium nitrate (CAN) supported on silica/NaBrO₃,²⁰ H₂O₂/*N*-hydroxysuccinimide,²¹ these methods suffer from some disadvantages like long reaction times, expensive reagents and catalysts, contamination of metallic reagents, difficulties in isolation of products, and formation of over-oxidation products.

In order to improve above-mentioned limitations and in continuation of our ongoing programs to introduce new reagents we became interested to apply a new catalytic method for the conversion of sulfides to the sulfoxides. Recently we have published a few reports on the oxidation of sulfides to the sulfoxides *via in situ* generation of bromonium ion (Br⁺), which is produce by treatment of metal nitrate or nitrite in the presence of an acidic source.²²⁻²⁷ Therefore, herein we decided to introduce a metal-free media for the production of bromonium ion (Br⁺) for the selective oxidation of sulfides to the sulfoxides by guanidinium nitrate, silica sulfuric acid and catalytic amounts of ammonium bromide in the presence of wet SiO₂ (50%

w/w). Consequently, a variety of aliphatic and aromatic sulfides **1** were subjected to the oxidation reaction to the corresponding sulfoxides **2** using guanidinium nitrate **I**, silica sulfuric acid **II** and catalytic amounts of NH₄Br **III** in the presence of wet SiO₂ (50% w/w) in dichloromethane at room temperature with good to moderate yields (Scheme 1 and Table 1).

Sulfoxidation reaction has been heterogeneously performed under mild conditions. All reagents and catalyst are insoluble in the reaction solvent. Consequently, sulfoxides easily produced *via* mixing of a sulfide, guanidinium nitrate, silica sulfuric acid, wet SiO₂ and a 5% mol of ammonium bromide; then stirring of this mixture at room temperature. Pure products can be easily isolated from the reaction media by washing the reaction mixture with dichloromethane, simple filtration and evaporation of dichloromethane.

As is evident from Table 1 the good range of turn over number (TON), (i.e. 5.40 to 19.60) of ammonium nitrate as catalyst is observed. To investigate the catalytic role of NH₄Br, as catalyst, 4-chlorophenyl methyl sulfide was subjected to the oxidation reaction in the absence of this agent as standard model. Surprisingly, 4-chlorophenyl methyl sulfoxide was obtained only in 7% yield after 24 hours (Table 1, entry 4). Also to show the role of silica sulfuric acid as acidic source of this procedure, same sulfide was subjected to sulfoxidation in the absence of acid. Interestingly, no sulfoxide product was observed after 24 h (Table 1, entry 5).

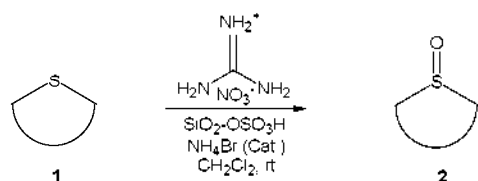
To consider chemoselectivity in the described system allyl methyl sulfide was converted successfully to allyl methyl sulfoxide in 85% yield and carbon-carbon double bond was intact in the course of reaction (Table 1, entry 16).

In order to investigate more selectivity of our system thianthrene was homoselectively oxidized to the thianthrene mono sulfoxide that is only one sulfur moiety took place in the sulfoxidation reaction.

Experimental Section

General. Chemicals were purchased on Fluka, Merck and Aldrich chemical companies. The oxidation products were characterized by comparison of their spectral (IR, ¹H NMR, or ¹³C NMR) and physical data with authentic samples.

Oxidation of 4-chlorophenyl methyl sulfide to 4-chlorophenyl methyl sulfoxide by guanidinium nitrate and silica



Scheme 1

Table 1. Oxidation of sulfides **1** to the corresponding sulfoxides **2** using guanidinium nitrate **I**, silica sulfuric acid **II** and catalytic amounts of NH_4Br **III** in the presence of wet SiO_2 (50% w/w) in dichloromethane at room temperature

Entry	Substrate	Product	Substrate/Reagents/Catalyst ^a			Time (Min)	Yield (%) ^b	TON
			I	II	III			
1			2	0.3	0.05	60	80	16.0
2			2	0.3	0.05	50	97	19.4
3			2	0.3	0.05	45	97	19.4
4			2	0.3	-	24h	7 ^c	-
5			2	-	0.05	24h	No reaction	-
6			2	0.3	0.05	45	92	18.4
7			2	0.3	0.05	70	93	18.6
8			2	0.3	0.05	55	82	16.4
9			2	0.4	0.05	19h	98	19.6
10			2	0.3	0.05	140	96	19.2
11			2	0.3	0.05	55	94	18.8
12			2	0.3	0.05	25	27	5.4
13	$\text{C}_n\text{-H}_{2n+2}\text{-S-C}_m\text{-H}_{2m}$	$\text{C}_n\text{-H}_{2n+2}\text{-S(=O)-C}_m\text{-H}_{2m}$	2	0.3	0.05	85	97	19.4
14			2	0.3	0.05	30	89	17.8
15			2	0.3	0.05	30	98	19.6
16			2	0.3	0.05	390	85	17.0

^aI and III refer to mmol of guanidinium nitrate and ammonium bromide, respectively; II refers to gram of silica sulfuric acid; Substrate : wet SiO_2 = 1 mmol : 0.2 g. ^bIsolated yield. ^cSulfoxide isolated by TLC.

sulfuric acid in the presence of ammonium bromide as catalyst.

To a mixture of 4-chlorophenyl methyl sulfide (0.158 g, 1 mmol), wet SiO_2 (0.2 g), guanidinium nitrate (0.244 g, 2 mmol) and ammonium bromide (0.005 g, 0.05 mmol) in CH_2Cl_2 (10 mL), silica sulfuric acid (0.3 g) was added. The resulting mixture was stirred at room temperature for 45 min (the reaction progress was monitored by TLC) and then filtered. The residue was washed with CH_2Cl_2 (20 mL). Anhydrous Na_2SO_4 (3 g) was added to the filtrate and filtered off after 20 min. Finally CH_2Cl_2 was evaporated and 4-chlorophenyl methyl sulfoxide obtained in 97 % yield (0.169 g). ¹H-NMR (200

MHz, CDCl_3) δ 7.47-7.63 (dd, J = 14.0, 8.6 Hz, 4H), 2.75 (s, 3H); ¹³C NMR (50 MHz, CDCl_3) δ 143.8, 137.1, 129.5, 125.0, 43.7.

Selected representative spectral data.

4-Thianthrene mono sulfoxide: ¹H-NMR (400 MHz, CD_3SOCD_3) δ 7.80-7.84 (m, 2H), 7.65-7.68 (m, 1H), 7.55-7.58 (m, 1H); ¹³C NMR (100 MHz, CD_3SOCD_3) δ 141.2, 130.9, 129.8, 129.3, 128.2, 124.7.

Methyl 3-(methylsulfinyl)propanoate: ¹H-NMR (90 MHz, CDCl_3) δ 3.70 (s, 3H), 3.33 (t, 2H), 2.84-2.91 (m, 5H); IR (KBr) $\bar{\nu}$ 1017, 1245, 1376, 1461, 1632, 1734, 2855 cm^{-1} .

Allyl methyl sulfoxide: ^1H NMR (200 MHz, CD_3SOCD_3) δ 5.75-5.97 (m, 1H), 5.31-5.39 (m, 2H), 3.34-3.62 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (50 MHz, CD_3SOCD_3) δ 127.5, 123.3, 56.5, 37.4.

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