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Catalytic Oxidation of Sulfides to Sulfoxides Using Aluminium Hydrogen Sulfate, Sodium Nitrite and Catalytic Amounts of Metal Bromide

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A catalytic, chemoselective and environmentally friendly procedure for the oxidation of sulfides is described. A wide range of aliphatic or aromatic sulfides were successfully oxidized to the corresponding sulfoxides using $NaNO_2$, $Al(HSO_4)_3$ and a catalytic amount of KBr or NaBr in the presence of wet SiO_2 (50% w/w) in CH_3CN under heterogeneous conditions in moderate to high yields.

Keywords: Sulfides, Sulfoxides, Homoselectivity, Metal bromide, Heterogeneous

INTRODUCTION

Metal hydrogen sulfates have attracted attention of organic chemists during the last decade. In addition, the stability and reasonable prices, heterogeneous nature of the reactions, high yields of the products, short reaction times, and reusability are among other important advantages of metal hydrogen sulfates [1].

Nowadays, most research is focused on the more versatile, more selective and more reactive catalysts [2]. 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 [3].

Sulfoxidation reactions are of significant importance in organic chemistry, medicinal chemistry, and drug metabolism [4]. Selective oxidation of sulfides to the corresponding sulfoxides remains a challenge and is interesting because of the importance of sulfoxides as synthetic intermediates in the synthesis of biological and medicinal compounds [5-7]. Additionally, some of biologically active sulfoxides play an important role as therapeutic agents such as anti-ulcer [8,9], antibacterial [10], anti-atherosclerotic [11-13] and so on.

In parallel with a good number of reports employing conventional oxidizing media for this transformation [14-29], search for new catalysts is still actively pursued to address the problems like effluent pollution, loss of selectivity and tedious workup procedures [30]. Sulfoxidation of sulfides by a metal-free chemoselective oxidation by hydrogen peroxide catalyzed by the *in situ* generated dodecyl hydrogen sulfate in the absence of any organic co-solvent as an environmentally friendly process is reported [31].

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The oxidation products were characterized in comparison with their spectral (IR, ^{1}H NMR, and ^{13}C NMR) and physical data with authentic samples.

Oxidation of Dibenzyl Sulfide to Dibenzyl Sulfoxide (General Procedure)

KBr (0.006 g, 0.05 mmol) was added to a solution of dibenzyl sulfides (0.214 g, 1 mmol) and wet SiO_2 (0.3 g) in

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CH_3CN (5 ml), followed by addition of $Al(HSO_4)_3$ (0.603 g, 1.1 mmol) and $NaNO_2$ (0.138 g, 2 mmol). The resulting reaction 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). The filtrates were combined and dried over anhydrous Na_2SO_4 (1.5 g) which, after filtration and evaporation of the solvent, gave dibenzyl sulfoxides in 0.216 g, 94% yield; m.p.: 131-134 ºC (Lit. 132-134 ºC [32]).

RESULTS AND DISCUSSION

In continuation of our studies on the application of new oxidizing reagents in the organic transformations [33-38], we became interested in the use of a novel oxidizing system, based on the *in situ* generation of X^+, for the selective oxidation of sulfides to sulfoxides.

For this purpose, catalytic amounts of sodium or potassium halides in the presence of $Al(HSO_4)_3/NaNO_2$ and wet SiO_2 in CH_3CN at room temperature was examined. The results are tabulated in Table 1.

Subsequently, to consider solvent effect, we screened different solvents for the oxidation of benzyl phenyl sulfide as model reaction. As it can be seen from Table 2 acetonitrile is the best solvent in terms of activity and selectivity (Table 2), therefore all oxidation reactions were performed in acetonitrile.

With optimized experimental conditions for benzyl phenyl sulfide in hand, we investigated sulfoxidation reactions with a variety of aliphatic and aromatic sulfides (Scheme 1 and Table 3).

The catalytic oxidation procedure is very simple and the products are easily isolated from the reaction media, because reactions are performed under completely heterogeneous conditions; therefore products can be easily obtained by simple filtration and evaporation of solvent.

Regarding the role of $Al(HSO_4)_3$ in the described system, it was revealed that sulfoxidation reaction did not perform in the absence of $Al(HSO_4)_3$, which means that the presence of acid is necessary in this reaction media (Table 3, entry 3). In addition to aluminum hydrogen sulfate, we examined a variety of metal hydrogen sulfates in the oxidation of benzyl phenyl sulfide, as typical example, in the presence of sodium nitrite and a catalytic amount of NaBr (Table 4). Thus we can apply different metal hydrogen sulfates instead of $Al(HSO_4)_3$ in this transformation.

Table 1. Oxidation of Benzyl Phenyl Sulfide by $Al(HSO_4)_3$, $NaNO_2$ and Catalytic Amounts of Sodium and Potassium Iodides and Bromides in the Presence of Wet SiO_2 (50% w/w)[a] in CH_3CN at Room Temperature

Entry	Catalyst	Time (h)	Yield (%)[b]
1	NaCl	8	-[c]
2	NaBr	25 min	99
3	NaI	8	-[c]
4	KBr	30 min	97
5	KI	8	-[c]
5	KCl	8	-[c]

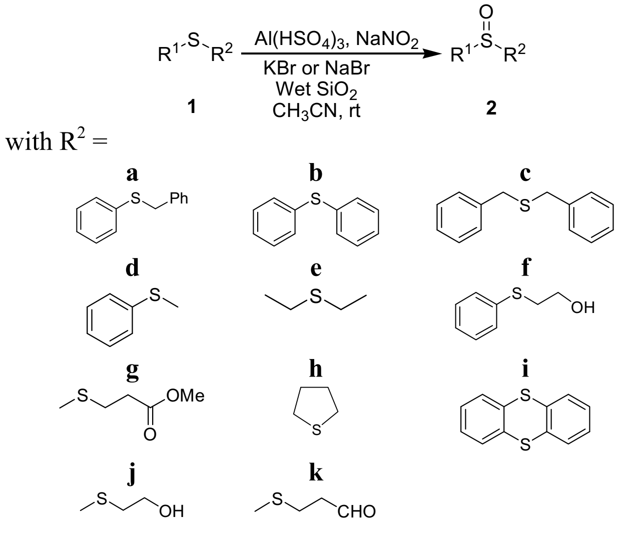
[a] Substrate/$Al(HSO_4)_3$/$NaNO_2$/MX/wet SiO_2:1:0.67:2:0.05 (mmol):0.3 g. [b] Isolated yield. [c] Reaction didn't complete.

Table 2. Oxidation of Benzyl Phenyl Sulfide by $Al(HSO_4)_3$, $NaNO_2$ and Catalytic Amounts of KBr in the Presence of Wet SiO_2 (50% w/w) in Different Solvents[a]

Entry	Solvent	Time (h)	Yield (%)[b]
1	Acetonitrile	30 min	98
2	Acetone	22	-[c]
3	Chloroform	20	-[d]
4	Dichloromethane	110 min	95
5	*n*-Hexane	23	-[c]
6	Methyl acetate	22	-[c]
7	Ethanol	22	-[d]

[a] Substrate/$Al(HSO_4)_3$/$NaNO_2$/KBr/wet SiO_2:1:0.67:2:0.05 (mmol):0.3 g. [b] Isolated yield. [c] Reaction didn't complete. [d] No reaction.

Also to show the catalytic role of KBr and NaBr in the described system, benzyl phenyl sulfide was subjected to the oxidation reaction without the catalyst. The reaction didn't complete within 20 h with the formation of sulfone as a



Scheme 1

byproduct (Table 3, entry 4). By this oxidizing system, thiantrene was homoselectively oxidized to thianthrene monosulfoxide (Table 3, entries 19 and 20, Scheme 2). This result is in almost full agreement with our previously reports [33-35].

Moreover, to show the chemoselectivity of the described system, two sulfides containing alcoholic group were subjected to the sulfoxidation reaction, but alcohol oxidation did not occur under the mentioned conditions, and primary hydroxyl groups remained intact during the reaction (Table 3, entries 13,14, 21 and 22, and Scheme 3).

A mechanism is also provided for the oxidation of sulfides to sulfoxides in Scheme 4 based on our previously reported works [33-35].

In summary, we report here an efficient method for the selective oxidation of sulfides to sulfoxides under completely

Table 3. Oxidation of Sulfides **1** to the Corresponding Sulfoxides **2** Using $Al(HSO_4)_3$ **I**, $NaNO_2$ **II** and Catalytic Amounts of KBr **III** or NaBr **IV** in the Presence of Wet SiO_2 (50% w/w) in Acetonitrile at Room Temperature

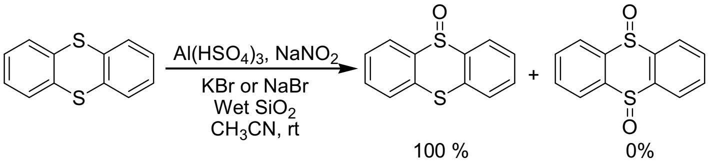
Entry	Substrate	Product	Substrate/Reagent/Catalysts[a]				Time (min)	Yield (%)[b]
			I	II	III	IV		
1	**1a**	**2a**	0.67	2	0.05	--	30	97
2	**1a**	**2a**	0.67	2	--	0.05	25	99
3	**1a**	**2a**	--	2	0.05	--	24 h	--[c,d]
4	**1a**	**2a**	0.67	2	--	--	20 h	--[d,e]
5	**1b**	**2b**	0.67	2	0.05	--	300	97
6	**1b**	**2b**	0.67	2	--	0.05	230	95
7	**1c**	**2c**	0.67	2	0.05	--	45	94
8	**1c**	**2c**	0.67	2	--	0.05	30	96
9	**1d**	**2d**	0.67	2	0.05	--	55	96
10	**1d**	**2d**	0.67	2	--	0.05	50	98
11	**1e**	**2e**	0.67	2	0.05	--	25	97
12	**1e**	**2e**	0.67	2	--	0.05	15	91
13	**1f**	**2f**	1.00	3	0.10	--	220	95
14	**1f**	**2f**	1 .00	3	--	0.10	205	97
15	**1g**	**2g**	0.67	2	0.05	--	40	98
16	**1g**	**2g**	0.67	2	--	0.05	36	99
17	**1h**	**2h**	0.67	2	0.05	--	25	93
18	**1h**	**2h**	0.67	2	--	0.05	20	82
19	**1i**	**2i**	0.67	2	0.05	--	205	98
20	**1i**	**2i**	0.67	2	--	0.05	220	90
21	**1j**	**2j**	0.67	2	0.05	--	80	93
22	**1j**	**2j**	0.67	2	--	0.05	75	88
23	**1k**	**2k**	0.67	2	0.05	--	60	72
24	**1k**	**2k**	0.67	2	--	0.05	45	98

[a]Substrate:wet SiO_2 = 1 mmol:0.3 g. [b]Isolated yield. [c]Without $Al(HSO_4)_3$. [d]No reaction. [e]Without KBr and NaBr.

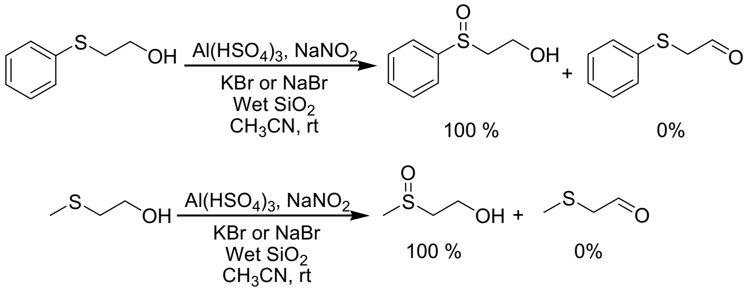
Table 4. Oxidation of Benzyl Phenyl Sulfide with Metal Hydrogen Sulfates, $NaNO_2$ and Catalytic Amounts of NaBr in the Presence of Wet SiO_2 (50% w/w) in Acetonitrile at Room Temperature

Entry	$M(HSO_4)_n$	mmol of $M(HSO_4)_n$[a]	Time (min)	Yield (%)[b]
1	$Zn(HSO_4)_2$	1	35	99
2	$Zr(HSO_4)_4$	0.5	25	97
3	$NaHSO_4$	2	25	90
4	$KHSO_4$	2	14 h	95

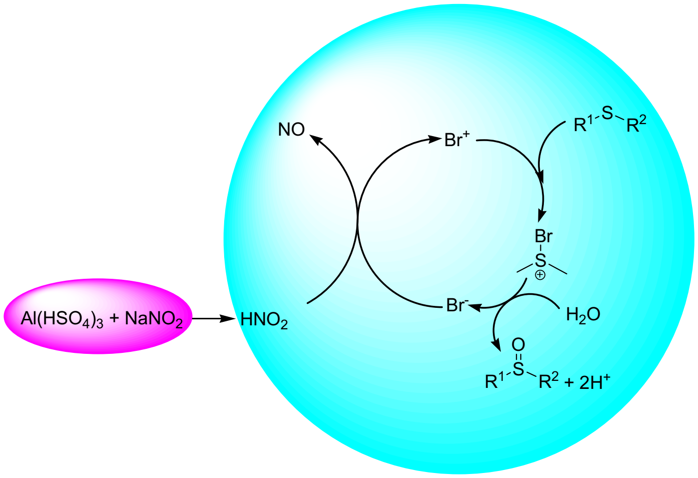
[a] Substrate:$NaNO_2$:KBr:wet SiO_2 = 1 mmol:2 mmol:0.05 mmol:0.3 g. [b] Isolated yield.



Scheme 2



Scheme 3



Scheme 4

heterogeneous conditions with good to excellent yields. Furthermore, this method exhibits substrate versatility, mild reaction conditions, and easy and clean work-up of products.

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