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ORIGINAL PAPER

Ferric nitrate in the presence of catalytic amounts of KBr or NaBr: an efficient and homoselective catalytic media for the selective oxidation of sulfides to sulfoxides

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Abstract A mild, efficient, and highly selective oxidation method of sulfides to sulfoxides using $Fe(NO_3)_3 \cdot 9H_2O$ and catalytic amounts of KBr or NaBr in the presence of wet SiO_2 (50% *w/w*) has been developed. A variety of aliphatic and aromatic sulfides were selectively oxidized at room temperature in good to excellent yields.

Keywords Homoselectivity · Sulfide · Ferric nitrate · KBr · NaBr · Oxidation

Introduction

An important aspect of clean technology is the use of environmentally friendly catalysts [1]. The development of efficient and new catalytic systems for various organic transformations is an active research area aiming at further improvements towards milder reaction conditions [2]. The selective oxidation of sulfides to sulfoxides is an important reaction both in industrial processes and in basic research [3]. Sulfoxides are useful synthetic intermediates in the synthesis of drugs and natural products [4–6]. Sulfoxides have also been used extensively in C–C bond-forming, molecular rearrangements and functional group transformations [7–11].

Although a number of methods for sulfoxidation have emerged in the recent years, such as H_2O_2/Mn(III) [12], stabilized iodine-2-iodoxybenzoic acid (SIBX) [13], immobilized vanadyl alkyl phosphonate/$NaBrO_3$/TBHP/H_2O_2 [14], PhIO/Mn(III) complexes [15], H_2O_2/bisflavinium perchlorate [16], amberlyst 15/H_2O_2 [17], 9- and 27-armed tetrakis(diperoxotungsto)phosphate-cored dendrimers/H_2O_2 [18], vanadium(IV) complexes of dibromo- and diiodo-functionalized chiral Schiff bases [19], magnesium monoperoxyphthalate (MMPP) [20], NBS/β-cyclodextrine [21], silica-based tungstate/H_2O_2 [22], pyridinium tribromide [23], $(Bu_4N)_3[PMo_{12}O_{40}]$/FAp/urea–$H_2O_2$ [24], carboxypyridinium chlorochromate/$AlCl_3$ [25], $(Bu_4N)_2S_2O_8$ [26], and MoO_2Cl_2/H_2O_2 [27], low selectivity, long reaction times, low yields of products, toxicity, expensive reagents and catalysts, and overoxidation to sulfones are still serious obstacles for this transformation.

Results and discussion

To overcome the above-mentioned disadvantages and in continuation of our ongoing program on the functionalization of organic compounds [28–38], we became interested in the use of new catalytic media, based on the in situ generation of Br^+, for the selective oxidation of sulfides to sulfoxides.

Initially, we screened different solvents for the oxidation of dibenzyl sulfide as our model reaction. We found that dichloromethane is the best solvent in terms of activity and selectivity (Table 1).

We wish to report here the selective oxidation of different types of sulfides **1** to the corresponding sulfoxides **2**

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using $Fe(NO_3)_3{\cdot}9H_2O$ (**I**) and catalytic amounts of KBr (**II**) and/or NaBr (**III**) in the presence of wet SiO_2 (50% *w*/*w*) in dichloromethane at room temperature with good to excellent yields (Scheme 1; Table 2).

As can be seen from Table 2, the reaction time increases in the absence of wet SiO_2 as a source of H_2O (Table 2, entries 8, 11, 12). Also, to show the catalytic role of KBr and NaBr in the described system, dibenzyl sulfide (as a typical example) was subjected to sulfoxidation without potassium and sodium bromide; however, the reaction did not complete after 240 min and a sulfone impurity was observed (Table 2, entry 7).

It is of interest that an excellent homoselectivity was observed in the oxidation of thianthrene. We wish to introduce the term "homoselectivity" in this article. We think that this keyword is suitable to be applied in special reactions. When there are two or more identical functional groups in a molecule, only one of them reacts selectively in the course of the reaction; this selectivity can be called homoselectivity. This oxidizing system allowed the homoselective oxidation of thianthrene to thianthrene monosulfoxide (Table 2, entries 21 and 22; Scheme 2).

To show the chemoselectivity of the described system, two sulfides containing a hydroxy group were subjected to

Table 1 Oxidation of dibenzyl sulfide with $Fe(NO_3)_3{\cdot}9H_2O$ and catalytic amounts of KBr in the presence of wet SiO_2 (50% *w*/*w*) in different solvents[a]

Entry	Solvent	Time/min	Yield[b]/%
1	Acetonitrile	60	91
2	Acetone	300	–[c]
3	Chloroform	45	95
4	Dichloromethane	15	95
5	*n*-Hexane	100	–[d]
6	Ethyl acetate	300	–[c]

[a] Substrate/$Fe(NO_3)_3{\cdot}9H_2O$/KBr/wet SiO_2: 1:1.2:0.05 (mmol):0.3 g

[b] Isolated yield

[c] No reaction

[d] Reaction completed but an equal mixture of sulfone and sulfoxide was observed

Table 2 Oxidation of sulfides **1** to the corresponding sulfoxides **2** using $Fe(NO_3)_3{\cdot}9H_2O$ (**I**) in the presence of catalytic amounts of KBr (**II**) or NaBr (**III**) in dichloromethane at room temperature

Entry	Substrate	Product	Substrate/ reagents/ catalysts[a]			Time/min	Yield[b]/%
		Reference	**I**	**II**	**III**		
1	**1a**	**2a**	1.2	0.05	–	90	89
2	**1a**	**2a**	1.2	–	0.05	95	84
3	**1b**	**2b**	1.5	0.3	–	360	63[c]
4	**1b**	**2b**	1.5	–	0.3	360	84[c]
5	**1c**	**2c**	1.2	0.05	–	15	95
6	**1c**	**2c**	1.2	–	0.05	15	98
7	**1c**	**2c**	1.2	–	–	240	–[d, e]
8	**1c**	**2c**	1.2	0.05	–	110	92[f]
9	**1d**	**2d**	1.2	0.05	–	20	98
10	**1d**	**2d**	1.2	–	0.05	15	96
11	**1d**	**2d**	1.2	0.05	–	65	98[f]
12	**1d**	**2d**	1.2	–	0.05	70	98[f]
13	**1e**	**2e**	1.2	0.05	–	20	98
14	**1e**	**2e**	1.2	–	0.05	20	98
15	**1f**	**2f**	1.2	0.05	–	40	83
16	**1f**	**2f**	1.2	–	0.05	95	95
17	**1g**	**2g**	1.2	0.05	–	10	87
18	**1g**	**2g**	1.2	–	0.05	15	84
19	**1h**	**2h**	1.2	0.05	–	240	–[g]
20	**1h**	**2h**	1.2	–	0.05	240	–[g]
21	**1i**	**2i**	1.2	0.05	–	140	90
22	**1i**	**2i**	1.2	–	0.05	130	88
23	**1j**	**2j**	1.4	0.2	–	20	95
24	**1j**	**2j**	1.4	–	0.2	35	90
25	**1k**	**2k**	1.2	0.05	–	40	73
26	**1k**	**2k**	1.2	–	0.05	40	78

[a] Substrate:wet SiO_2 = 1 mmol:0.3 g

[b] Isolated yield

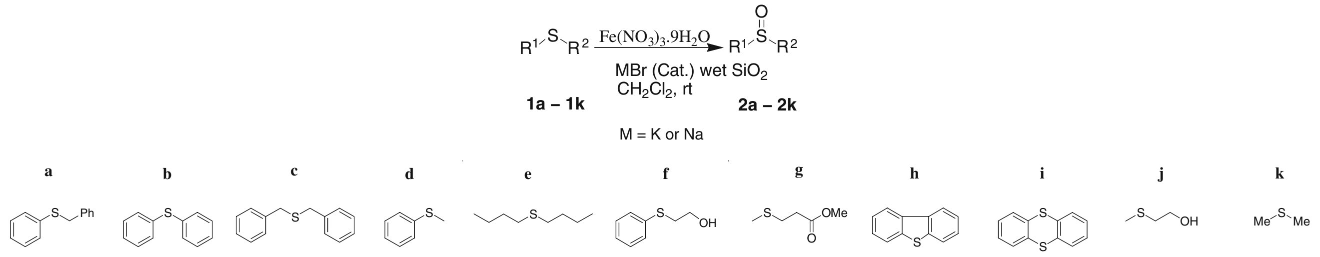
[c] GC yield

[d] In the absence of KBr and NaBr

[e] Reaction did not complete and a mixture of sulfone and sulfoxide was observed

[f] Without wet SiO_2

[g] No reaction



Scheme 1

Scheme 2

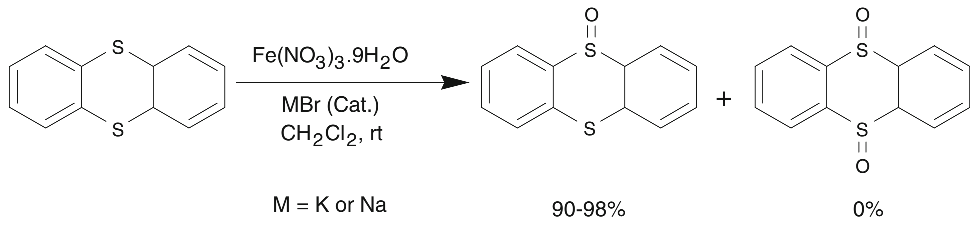


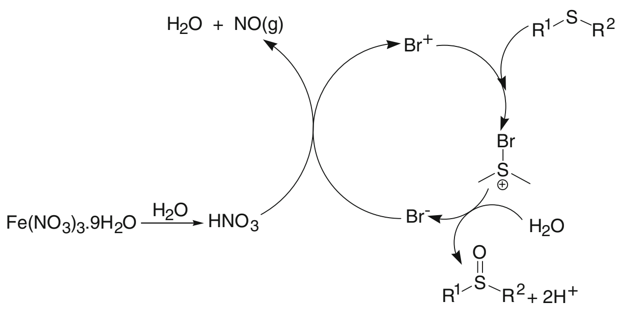
Table 3 Efficiency comparison of various oxidizing systems for the oxidation of methyl phenyl sulfide

Entry	Catalyst	Oxidant	Time/min	Yield[a]/%	Reference
1	NaBr	$Fe(NO_3)_3 \cdot 9H_2O$	20	98	This work
2	KBr	$Fe(NO_3)_3 \cdot 9H_2O$	15	96	This work
3	Silica-based ammonium tungstate	H_2O_2 (aq)	1.5 h	82	[22]
4	Dodecyl hydrogen sulfate	H_2O_2 (aq)	5	92	[39]
5	$HAuCl_4 \cdot 4H_2O$	H_2O_2 (aq)	60	99[b, c]	[40]
6	*n*-Bu_4NBr	NaOCl	30	93	[41]
7	Human hemoglobin	H_2O_2 (aq)	30	96	[42]
8	$Ti(O^iPr)_4$	(*S*)-1-phenylethyl hydroperoxide	6 h	79[b]	[43]
9	$PhSO_2N{=}CHPhNO_2$-*p*	Oxone	30	95[c]	[44]
10	CAN	$NaBrO_3$	13	99	[45]

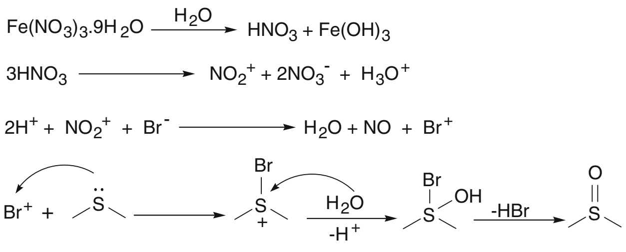
[a] Isolated yield

[b] Conversion

[c] Trace impurity of sulfone was observed



Scheme 3



Scheme 4

the sulfoxidation reaction, and the primary hydroxyl group remained intact in the course of the reaction (Table 2, entries 15–16 and 23–24).

To show the efficiency of the described system in comparison with previously reported procedures in literature, we compared our obtained results for the oxidation of methyl phenyl sulfide with the best of the well-known data from literature, as shown in Table 3.

A plausible mechanism for this oxidation is shown in Scheme 3, based on a reported pathway in literature [31, 46], our observations, and the obtained results.

Initially, hydrolysis of ferric nitrate generates HNO_3 in situ; subsequently, auto ionization of nitric acid generates in situ nitronium ion (NO_2^+). Then, Br^- can be oxidized and generates Br^+ in situ. The final step of oxidation involves a nucleophilic attack of sulfur on the Br^+, followed by concerted oxygen transfer from water to sulfur atoms of sulfonium bromide to give sulfoxides (Scheme 4).

One of the observed pieces of evidence for this mechanism is the evolution of NO gas from the reaction vessel that can be converted to the nitrogen brown-color oxide compounds, which can be observed on the top of the reaction solution.

In conclusion, we have reported a catalytic, simple, and mild method for the synthesis of sulfoxides by the oxidation of sulfides with catalytic-generated Br^+. This method offers the advantage of shorter reaction times, high chemoselectivity, and easy workup. We believe that the present methodology could be an important addition to the existing methodologies.

Experimental

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The oxidation products were characterized by the comparison of their spectral (IR, ^{1}H NMR, and ^{13}C NMR) and physical data with authentic samples [25, 47–50].

*Oxidation of dibutyl sulfide (**1e**) to dibutyl sulfoxide (**2e**) by $Fe(NO_3)_3{\cdot}9H_2O$/KBr as an example*

KBr (0.006 g, 0.05 mmol) was added to a solution of 0.146 g dibutyl sulfide **1e** (1 mmol) in 5 cm^3 CH_2Cl_2, followed by the addition of 0.484 g $Fe(NO_3)_3{\cdot}9H_2O$ (1.2 mmol) and 0.3 g wet SiO_2. 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 20 cm^3 CH_2Cl_2 . Anhydrous Na_2SO_4 (1.5 g) was added to the filtrate and then filtered off after 20 min. Finally, CH_2Cl_2 was removed and the yield was 0.158 g (98%).

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