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Selective and efficient oxidation of sulfides to sulfoxides using ammonium cerium (IV) nitrate in the presence of a catalytic amount of KBr or NaBr

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Abstract A wide range of aliphatic or aromatic sulfides are selectively oxidized to the corresponding sulfoxides using ammonium cerium (IV) nitrate (*CAN*) and a catalytic amount of KBr or NaBr in the presence of wet SiO_2 in CH_2Cl_2 under heterogeneous conditions in moderate to high yields.

Keywords Sulfides; Sulfoxides; Ammonium cerium (IV) nitrate (*CAN*); Monoselectivity.

Introduction

The chemistry of sulfoxides has been attractive to organic chemists. The interest to the chemistry of sulfoxides is due to the fact that sulfoxides are important synthetic intermediates in the preparation of biologically and medicinally compounds [1–3]. Sulfoxides have been also used extensively in C–C bond-forming, molecular rearrangements, and functional group transformations [4–8].

Although many reagents are available for the oxidation of sulfides to the sulfoxides [9–30], the catalytic process with environmentally benign oxidants have become increasingly important. Also it is usually observed that sulfoxidation is sufferes by at least one of the following disadvantages: long reaction times, low selectivity, low yields of products, toxicity, expensive reagents and catalysts, *etc.* Furthermore, sulfoxides can undergo overoxidation to sulfones and therefore it is important that the catalyst has low reactivity towards the sulfoxides [31].

Results and discussion

To overcome the above mentioned disadvantages and in continuation of our studies on the application of oxidizing agents in organic transformations [32–38] we became interested in the use of a new oxidizing system, based on *in situ* generation of X^+ for the selective oxidation of sulfides to sulfoxides.

To find the best catalytic conditions for the oxidation of sulfides, a combination of different oxidants and catalytic amounts of KBr, NaBr, or NaCl, in the presence of wet SiO_2 (50% w/w) in dichloromethane at room temperature was examined, and the results are summarized in Table 1. As it can be seen in Table 1, the best choice is referred to ammonium cerium (IV) nitrate (*CAN*)/KBr or NaBr. Subsequently we screened different solvents for the oxidation of dibenzyl sulfide and found that dichloromethane is the best solvent in term of activity and selectivity (Table 2).

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Table 1 Comparison of different oxidants in oxidation of sulfides using catalytic amounts of a metal halide, in the presence of wet SiO_2 (50% *w*/*w*) in CH_2Cl_2 at room temperature

Entry	Substrate	Oxidizing system	Substrate/ oxidant/*MX*[a]	Time/h	Yield/%[b]
1	benzyl phenyl sulfide	$(NH_4)_2Ce(NO_3)_6 \cdot 2H_2O$/KBr	1:1.5:0.3	0.75	–[c]
2	benzyl phenyl sulfide	$(NH_4)_2Ce(NO_3)_6 \cdot 2H_2O$/KBr	1:1.1:0.15	1.5	–[d]
3	benzyl phenyl sulfide	$(NH_4)_2Ce(NO_3)_6 \cdot 2H_2O$/KBr	1:1.1:0.3	0.5	83
4	benzyl phenyl sulfide	$(NH_4)_2Ce(NO_3)_6 \cdot 2H_2O$/NaCl	1:1.1:0.3	2	–[e]
5	dibenzyl sulfide	$(NH_4)_2Ce(NO_3)_6 \cdot 2H_2O$/KBr	1:1.1:0.3	0.3	96
6	dibenzyl sulfide	$(NH_4)_2Ce(NO_3)_6 \cdot 2H_2O$/NaBr	1:1.1:0.3	0.3	89
7	dibenzyl sulfide	$(NH_4)_2Ce(NO_3)_6 \cdot 2H_2O$/NaCl	1:1.1:0.3	15	–[c]
8	benzyl phenyl sulfide	Oxone®/KBr	1:1.1:0.3	5	–[e]
9	benzyl phenyl sulfide	Oxone®/KBr	1:1.3:0.2	2.5	–[d]
10	dibenzyl sulfide	Oxone®/KBr	1:1.1:0.3	2.5	51[f]
11	dibenzyl sulfide	$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$/KBr	1:1.1:0.3	5	–[e]
12	dibenzyl sulfide	$KClO_3$/KBr	1:1.1:0.3	5	–[g]
13	dibenzyl sulfide	HIO_4/KBr	1:1.1:0.3	5	–[e]
14	dibenzyl sulfide	NH_4VO_2/KBr	1:1.1:0.3	2	–[g]
15	dibenzyl sulfide	$NaBO_2H_2O_2 \cdot 3H_2O$/KBr	1:1.1:0.3	3.5	–[g]
16	dibenzyl sulfide	Na_2WO_4/KBr	1:1.1:0.3	2	–[g]
17	dibenzyl sulfide	DABCO-DNODP/KBr	1:1.1:0.3	2	–[g]
18	dibenzyl sulfide	UHP/KBr	1:1.1:0.3	3	–[g]
19	dibenzyl sulfide	HIO_3/KBr	1:1.1:0.3	4	–[d]
20	dibenzyl sulfide	$(NH_4)_2S_2O_8$/KBr	1:1.1:0.3	3	–[g]
21	dibenzyl sulfide	$K_2S_2O_8$/KBr	1:1.1:0.3	3	–[g]
22	dibenzyl sulfide	Na_2O_2/KBr	1:1.1:0.3	3	–[g]

[a] Substrate: wet SiO_2 = 1 mmol: 0.3 g; [b] Isolated yield; [c] Reaction was completed but impurity of sulfone was observed; [d] Reaction did not complete and a mixture of sulfoxide and sulfone was observed; [e] Reaction did not complete and a few spots was observed on the TLC; [f] GC yield; [g] No reaction

Table 2 Oxidation of dibenzil sulfide using ammonium cerium(IV) nitrate *CAN* and catalytic amounts of KBr in the presence of wet SiO_2 (50% *w*/*w*)[a] in different solvents

Entry	Solvent	Time/min	Yield/%[b]
1	acetonitrile	105	–[c]
2	acetone	120	–[d]
3	chloroform	105	98
4	dichloromethane	20	96
5	*n*-hexane	120	–[d]

[a] Sub.:*CAN*:KBr:wet SiO_2 = 1 mmol:1.1 mmol:0.3 mmol: 0.3 g; [b] Isolated yield; [c] Reaction was completed but a few spots was observed on the TLC; [d] Reaction did not complete and a few spots was observed on the TLC

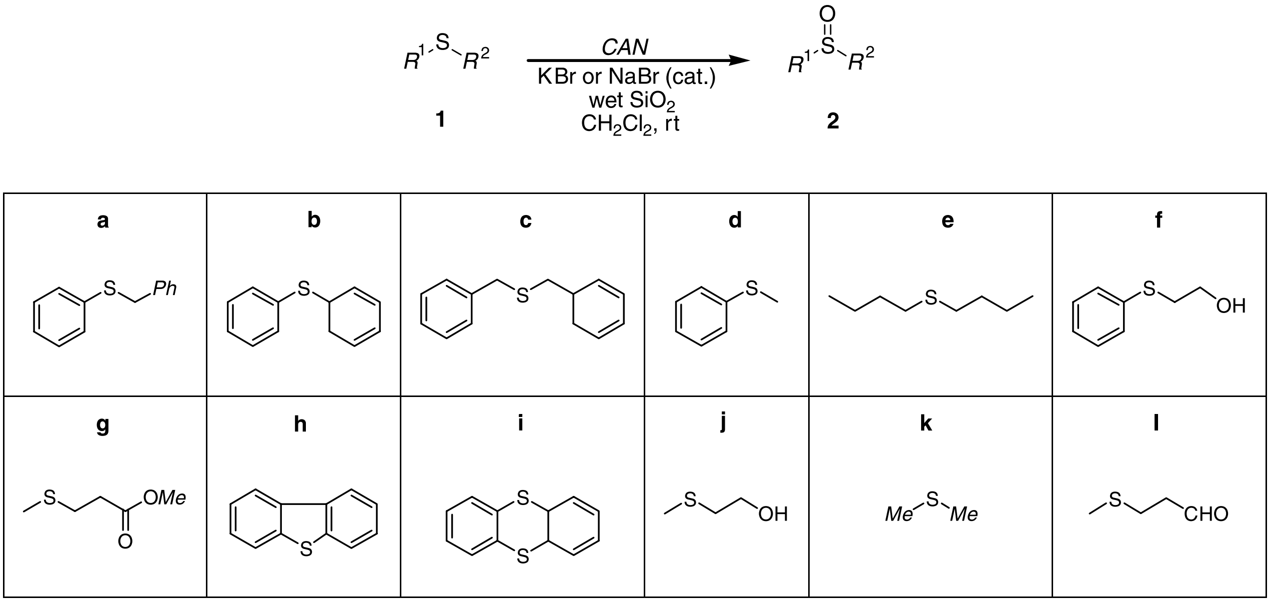
Eventually, we wish to report here the selective oxidation of different types of sulfides **1** to the corresponding sulfoxides **2** using *CAN* (**I**) and catalytic amounts of KBr (**II**) or NaBr (**III**) in the presence of wet SiO_2 (50% *w*/*w*) in dichloromethane at room temperature with good to excellent yields (Scheme 1 and Table 3).

To show the catalytic role of KBr and NaBr in the described system, benzyl-phenyl-sulfide was subjected to the oxidation without any KBr and NaBr. However, the reaction did not complete after 15 h and an impurity of sulfone was observed (Table 3, entry 2). Also we considered the role of wet SiO_2 in our system and found that sulfoxidation was not performed without this agent (Table 3, entry 3).

It is of interest that this oxidizing system was monoselectively oxidized thianthrene to thianthrene monosulfoxide (Table 3, entries 19, 20 and Scheme 2).

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

A plausible mechanism of this oxidation is shown in Scheme 4 based on reported pathway in Refs. [34, 39], our observations and obtained results.

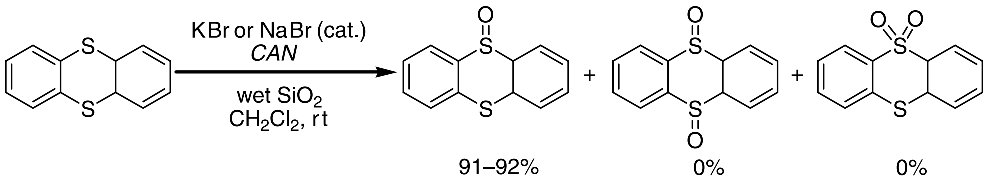


Scheme 1

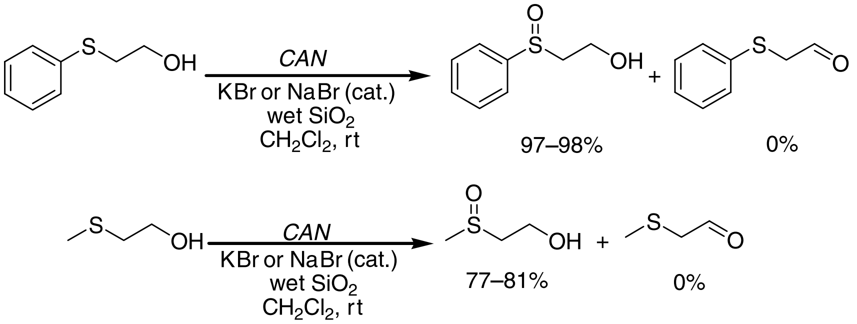
Table 3 Oxidation of sulfides **1** to the corresponding sulfoxides **2** using *CAN* (**I**) and catalytic amounts of KBr (**II**) or NaBr (**III**) in the presence of wet SiO_2 (50% *w*/*w*) in dichloromethane at room temperature

Entry	Substrate	Product	Substrate/reagent/catalysts[a]			Time/min	Yield/%[b]
			I	**II**	**III**		
1	**1a**	**2a**	1.1	0.3	–	35	83
2	**1a**	**2a**	1.1	–	–	15 h	–[c,d]
3	**1a**	**2a**	1.1	0.3	–	24 h	–[e,f]
4	**1a**	**2a**	1.1	–	0.3	35	93
5	**1b**	**2b**	1.1	0.3	–	6 h	96
6	**1b**	**2b**	1.1	–	0.3	6.5 h	88
7	**1c**	**2c**	1.1	0.3	–	20	96
8	**1c**	**2c**	1.1	–	0.3	20	89
9	**1d**	**2d**	1.1	0.3	–	30	98
10	**1d**	**2d**	1.1	–	0.3	15	98
11	**1e**	**2e**	1.1	0.3	–	25	98
12	**1e**	**2e**	1.1	–	0.3	20	85
13	**1f**	**2f**	1.1	0.3	–	25	97
14	**1f**	**2f**	1.1	–	0.3	80	98
15	**1g**	**2g**	1.1	0.3	–	15	98
16	**1g**	**2g**	1.1	–	0.3	20	89
17	**1h**	**2h**	1.1	0.4	–	5 h	46[g]
18	**1h**	**2h**	1.1	–	0.3	4.75 h	68[g]
19	**1i**	**2i**	1.1	0.3	–	80	92
20	**1i**	**2i**	1.1	–	0.3	95	91
21	**1j**	**2j**	1.1	0.3	–	10	81
22	**1j**	**2j**	1.1	–	0.3	25	77
23	**1k**	**2k**	1.1	0.3	–	20	67
24	**1k**	**2k**	1.1	–	0.3	20	74
25	**1l**	**2l**	1.1	0.3	–	15	79
26	**1l**	**2l**	1.1	–	0.3	30	81

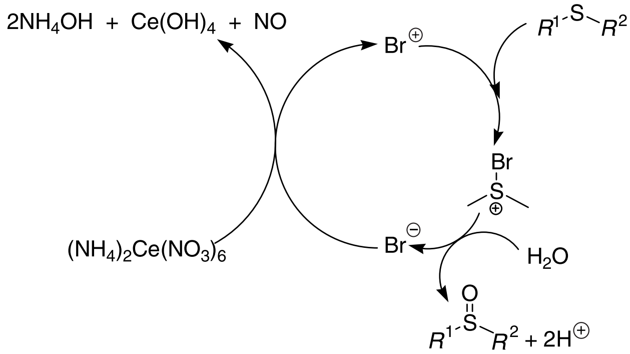
[a] Substrate: wet $SiO_2 = 1$ mmol: 0.3 g; [b] Isolated yield; [c] Reaction did not complete and impurity of sulfone was observed; [d] Without KBr and NaBr; [e] Without wet SiO_2; [f] No reaction; [g] GC yield



Scheme 2

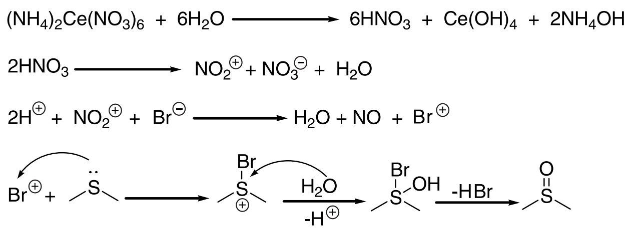


Scheme 3



Scheme 4

Reaction of ammonium cerium nitrate *CAN* with H_2O might *in situ* generates HNO_3. Subsequently, Br^+ can be produced *via* oxidation of bromide ion by nitric acid. The final step of oxidation involves a nucleophilic attack of sulfur on the Br^+ followed by concerted oxygen transfer from water to give sulfoxides (Scheme 5).



$$(NH_4)_2Ce(NO_3)_6 + 6H_2O \longrightarrow 6HNO_3 + Ce(OH)_4 + 2NH_4OH$$

$$2HNO_3 \longrightarrow NO_2^{\oplus} + NO_3^{\ominus} + H_2O$$

$$2H^{\oplus} + NO_2^{\oplus} + Br^{\ominus} \longrightarrow H_2O + NO + Br^{\oplus}$$

Scheme 5

In conclusion, we report here an efficient method for the selective oxidation of sulfides to sulfoxides under very mild heterogeneous conditions with good to high yields. Also chemoselectivity, the cheapness and availability of the reagents, easy and clean work-up, and high yields make this method attractive. 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 comparison of their spectral (IR, ^1H NMR, and ^{13}C NMR) and physical data with authentic samples [14, 40–44].

Oxidation of dibenzyl sulfides to dibenzyl sulfoxide

Potassium bromide (0.0357 g, 0.3 mmol) was added to a solution of 0.214 g dibenzyl sulfides (1 mmol) and 0.3 g wet SiO_2 in 10 cm^3 CH_2Cl_2 followed by addition of 0.603 g *CAN* I (1.1 mmol). 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 filtered off after 20 min. Finally, CH_2Cl_2 was removed and the yield was 0.222 g (96%).

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