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Oxidation of Sulfides to Sulfoxides by $NaBrO_3$-NH_4Cl in Aqueous Acetonitrile

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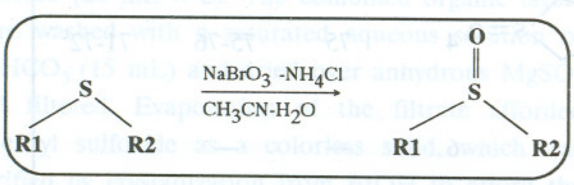
ABSTRACT: *$NaBrO_3$ combined with NH_4Cl is found to be an efficient reagent for the transformation of sulfides into sulfoxides in aqueous acetonitrile and under mild conditions.*

KEY WORDS: *Sulfide, Sulfoxide, Oxidation, Sodium bromate, Ammonium chlorid*

INTRODUCTION

Sulfoxide synthesis constitutes an important research area [1-7] as they are versatile building blocks in organic synthesis [8,9]. A great number of oxidizing agents can effect the conversion of sulfides into sulfoxides [10-15]. However, the susceptibility of sulfoxide to further oxidation narrows the choice of reagents for the oxidation of sulfides to sulfoxides. Introduction of new oxidants for the transformation of sulfides to sulfoxides under mild condition is of importance in synthetic organic chemistry. $NaBrO_3$ and $AgBrO_3$ have been used for the oxidation of varieties of organic compounds in the presence of Lewis acids in aprotic organic solvents [16]. Recently mixture of $NaBrO_3$ -NH_4Cl is used as efficient oxidant for the oxidation of alcohols [17]. In this paper oxidation of sulfides to sulfoxides using $NaBrO_3$ -NH_4Cl is reported.



This reagent is a cheap, safe and very convenient one for the oxidation reaction of sulfides, compared with other oxidizing agents.

Table 1, summarizes the results of various sulfide oxidation with $NaBrO_3$ -NH_4Cl to corresponding sulfoxides in good yields. Sulfones were not detected in the crude mixture, which indicates high selectivity of the present method.

Sodium bromate in the absence of NH_4Cl is also able to transform dialkyl sulfides to corresponding sulfoxides (entry 9-11), but this reagent alone is not capable of oxidizing aryl sulfide (entry 12-14).

To study the oxidation ability of $NaBrO_3$ -NH_4Cl, a few reaction is run by using $Bu_4NIO_4/AlCl_3$ [15], $Bi(NO_3)_3 . 5H_2O/HOAc$ [18], $Ba(MnO_4)_2$ [13] and $H_2O_2/MeCN/K_2CO_3/CH_3OH$ [19] (Table 2).

EXPERIMENTAL

All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. Melting points were determined in open capillaries using an

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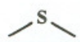
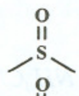
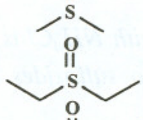
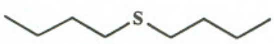
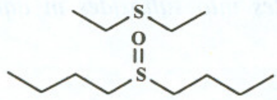
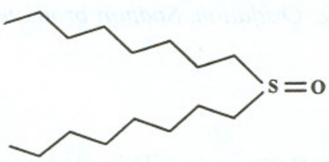
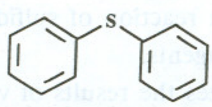
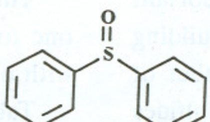
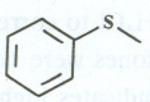
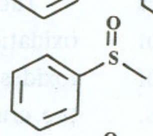
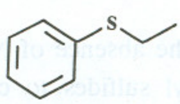
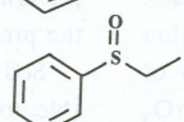
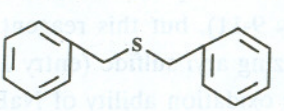
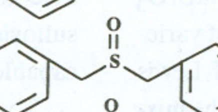
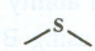
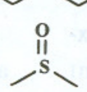
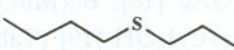
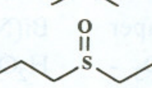
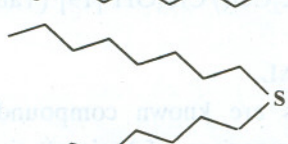
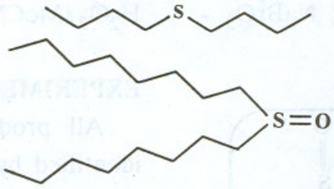
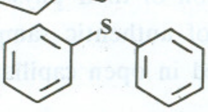
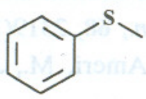
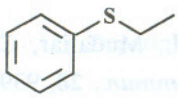
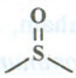
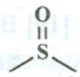
oil-bath and are uncorrected. IR spectra were recorded as neat films or as KBr pellets on a Shimadzu 470 spectrophotometer. ^{1}H NMR spectra were recorded at 90 MHz on a JEOL EX-90 instrument with $CDCl_3$ as solvent and Me_4Si as an internal standard. All sulfides were purchased from Fluka, Aldrich and Merck

Table 1: Oxidation of sulfide to sulfoxide compounds by $NaBrO_3$-NH_4Cl in acetonitrile-water (7:3 v/v) at 40°C

Entry	Substrate	Product	Reaction time (t/h)	Yield[a] (%)	m.p.(°C) or b.p.(°C) Found	m.p.(°C) or b.p.(°C) Report
1			2.5	95	190-192	189[b]
2			4	95	103-105	104[b]
3			3.5	90	28-30	32.6[b]
4			1.5	95	75-76	71-72[c]
5			30	85	73-74	70.5[d]
6			3	90	30-33	33-34[c]
7			4	90	147-148.13	146.13[c]
8			3.5	90	135-137	133-135[c]
9[e]			4	85	190-191	189[b]
10[e]			4	80	28-30.6	32.6[b]
11[e]			4	75	75-76	71-72[c]
12[e]		no reaction	6	—	—	

Continued

Entry	Substrate	Product	Reaction time (t/h)	Yield[a] (%)	m.p.(°C) or b.p.(°C) Found	Report
13[e]		no reaction	4	—	—	
14[e]		no reaction	4	—	—	
15[f]			8	—	—	

a) Yield refers to isolated product

b) From ref. 20

c) From ref. 21

d) From ref. 22

e) In the absence of NH_4Cl

f) Isolated sulfoxide without any transformation to sulfone

Table 2: Comparison of the results of $NaBrO_3$ -NH_4Cl with those obtained from $Bu_4NIO_4/AlCl_3$ (1) [15], $Bi(NO_3)_3.5H_2O/HOAc$ (2) [18], $Ba(MnO_4)_2$ (3) [13] and $H_2O_2/MeCN/K_2CO_3/CH_3OH$ (4) [19]

Entry	Substrate	Product	Yield % (h) $NaBrO_3$ -NH_4Cl	Yield %(h) reported by other methods 1	2	3	4
1	$(C_4H_9)_2S$	$(C_4H_9)_2SO$	90(3.45)	—	68(2)	—	84(0.5)
2	$C_6H_5SCH_3$	$C_6H_5SOCH_3$	90(3)	70(4)	—	—	82(2)
3	$(C_6H_5CH_2)_2S$	$(C_6H_5CH_2)_2SO$	90(3.5)	75(4)	85(4)	77(4)	—

Chemical Companies.

Oxidation of Dibenzyl Sulfide (entry 8)

Typical Procedure

Dibenzyl sulfide (1.072 g, 5 mmol) was added to a mixture of $NaBrO_3$ (0.755 g, 5 mmol) and NH_4Cl (0.400 g, 7.5 mmol) in aqueous acetonitrile (CH_3CN-H_2O; 7:3 v/v; 10 mL) and stirred at 40°C for 3.5 h. The resulting mixture was extracted with methylene chloride (20 mL × 2). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (15 mL) and dried over anhydrous $MgSO_4$ and filtered. Evaporation of the filtrate afforded dibenzyl sulfoxide as a colorless solid, which was purified by crystallization from EtOH to afford the desired product, yield, 1.037 g, (90%), m.p. 135-137°C (lit. 133-135°C), [22].

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