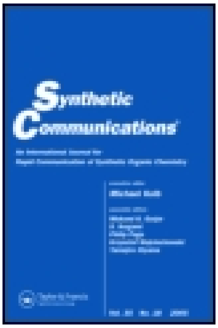

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$Bi(NO_3)_3.5H_2O$: A CONVENIENT REAGENT FOR SELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES

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ABSTRACT: $Bi(NO_3)_3.5H_2O$, a cheaply available, crystalline solid has been found to readily effect selective oxidation of a variety of sulfides to sulfoxides in acetic acid medium at room temperature in fair to good yields.

Organic sulfoxides are versatile synthons for C-C bond formations, functional group transformations and molecular rearrangements[1]. By far, the most popular method to prepare sulfoxides involves the selective oxidation of sulfides which can be accomplished by a variety of oxidants namely, hydrogen peroxide and its derivatives, halogens and electrophilic halogen carriers, nitrogen oxide derivatives, periodates and metal salts in high oxidation states[2]. Among newer methods, Zeolite-assisted and Ti-pillared montmorillonite catalysed selective oxidation of sulfides to sulfoxides has recently been reported[3]. However, problem of contamination from the over-oxidation products, sulfones, and the need to use expensive reagents often in greater than stoichiometric amounts and functional group incompatibility detract from their practical applications in many cases.

Since, a number of nitrogen oxide carriers such as HNO_3[4], $(NH_4)_2Ce(NO_3)_6$[5] and $Tl(NO_3)_3$[6] are known to oxidise sulfides, we thought it worthwhile to investigate the

Table: Selective oxidation of sulfides to sulfoxides by $Bi(NO_3)_3.5H_2O^a$

Entry	RSR' starting sulfides	RSOR' product sulfoxides	Time (h)	Yield^b (%)	mp. (°C)	lit. mp. (°C)
1.	$(C_6H_5CH_2)_2S$	$(C_6H_5CH_2)_2SO$	4	85	135-36	137.5[8]
2.	$(C_6H_5CH_2CH_2)_2S$	$(C_6H_5CH_2CH_2)_2SO$	7	80	70-71	70.2-70.4[9]
3.	$(n\text{-}C_4H_9)_2S$	$(n\text{-}C_4H_9)_2SO$	2	68	31-32	32.6[10]
4.	$C_6H_5SCH_2C_6H_5$	$C_6H_5SOCH_2C_6H_5$	6	78	123-24	124[11]
5.	$C_6H_5S(CH_2)_2C_6H_5$	$C_6H_5SO(CH_2)_2C_6H_5$	8	80	oil^c	-
6.	$4\text{-}CH_3C_6H_4SCH_2C_6H_5$	$4\text{-}CH_3C_6H_4SOCH_2C_6H_5$	8	75	134-35	135-36[12]
7.	$4\text{-}CH_3C_6H_4SCH_3$	$4\text{-}CH_3C_6H_4SOCH_3$	6	65	42-43	42-43[13]
8.	$C_6H_5SCH_2CO_2C_2H_5$	$C_6H_5SOCH_2CO_2C_2H_5$	24	50	oil^d	-
9.	$C_6H_5SCH(CH_3)_2$	$C_6H_5SOCH(CH_3)_2$	6	70	oil^e	-
10.	$(C_6H_5CO_2CH_2CH_2)_2S$	$(C_6H_5CO_2CH_2CH_2)_2SO$	8	70	83-85	83-85[14]
11.	$2\text{-}NO_2C_6H_4SCH_2C_6H_5$	No reaction	48	-	-	-
12.	$C_6H_5COCH_2SCH_2C_6H_5$	Decomposition products	8	-	-	-

a) All reactions uniformly conducted at room temperature in glacial acetic acid using 5 mmol each of the sulfide and $Bi(NO_3)_3.5H_2O$. b) yields refer to t.l.c. homogeneous products and are unoptimized. c) Lit[15]. ^{1}HNMR ($CDCl_3$) : δ 2.8-3.1(4H, m,-$C\underline{H}_2C\underline{H}_2$), 7.07.6 (10H, m, $\underline{H}$arom.). Anal. calcd. for $C_{14}H_{14}OS$: C, 73.04; H, 6.09; S, 13.91. Found : C, 73.55; H, 6.49; S, 14.18%. d) Lit[16]. IR (oil film): 1740, 1490, 1445, 1100, 1025 cm^{-1}. ^{1}HNMR ($CDCl_3$) : δ 1.3 (3H, t, $C\underline{H}_3CH_2$-), 3.8 (2H, s, $SC\underline{H}_2$-), 4.2 (2H, q, $CH_3C\underline{H}_2$-) 7.3-7.9 (5H, m, $\underline{H}$arom.). Anal. calcd. for $C_{10}H_{12}O_3S$: C, 56.60; H,5.66; S, 15.09. Found : C, 56.94; H, 5.31; S, 15.43. e) Lit[17]. ^{1}HNMR ($CDCl_3$) : δ 1.15 (6H, d, j=Hz, $-CH(C\underline{H}_3)_2$), 2.7 (1H, m, -$C\underline{H}(CH_3)_2$), 7.4 (5H, bs, $\underline{H}$arom.). Anal. calcd. for $C_9H_{12}OS$: C, 64.29; H, 7.14; S,19.09. Found : C, 64.03; H, 6.89; S,19.53.

potential of $Bi(NO_3)_3.5H_2O$ **1** for the oxidation of sulfides. We report in this article that the title reagent **1**, a commercially inexpensive, crystalline solid can indeed be employed for the selective oxidation of sulfides to sulfoxides as depicted in the generalized equation(1). Our results are collected in the Table. We first examined the oxidation of dibenzyl sulfide (entry 1) as a test case with an equimolar amount of **1** under different conditions. Acetic acid was found to be a solvent of choice giving quantitative conversion to a single product, dibenzyl sulfoxide (entry 1, 85% isolated yield) within 4h at room temperature.

$$\text{R-S-R}' + Bi(NO_3)_3.5H_2O\ \mathbf{(1)} \longrightarrow \text{R-SO-R}' \qquad (1)$$

To evaluate the general scope, a number of symmetrical and unsymmetrical sulfides, prepared following our micellar procedure[7], were submitted to oxidation with **1** in acetic acid for the time indicated in the Table. The isolated yields are fair to excellent and the work-up consists of diluting the reaction with water, neutralization with sat.$NaHCO_3$ and extraction with $CHCl_3$. The crude products obtained upon solvent removal were purified either by a short SiO_2 column chromatography or crystallization. However, the present procedure is not without limitations. For instance, 2-nitrophenyl phenylsulfide (entry 11) failed to react with **1** even after 48 h at room temperature and attempted oxidation of phenacyl benzylsulfide (entry 12) produced only decomposition products.

In summary, we have described a new application of **1** in the selective oxidation of a variety of sulfides to sulfoxides in preparatively acceptable yields.Despite some limitations, experimental simplicity, mild reaction conditions and low cost of the reagent makes this procedure generally useful for the preparation of sulfoxides.

Preparation of dibenzyl sulfoxide. General procedure: To a solution of dibenzyl sulfide (1.07gm., 5mmol) in glacial acetic acid (15 ml) was added $Bi(NO_3)_3.5H_2O$ (2.425gm., 5mmol) in small lots during 10 min. at room temperature. The reaction was accompanied by a mild exotherm and produced brownish vapours of nitrogen oxides. After 4h at room temperature whereby the t.l.c. showed complete consumption of the starting sulfide, the reaction mixture was diluted with cold water, neutralized with sat. $NaHCO_3$ and extracted with chloroform. The extract was dried over anhyd. Na_2SO_4 and concentrated to give a solid product. Crystallization from aq.ethanol afforded colourless crystals of dibenzyl sulfoxide (970 mg, 85% yield), mp 135-36 ^{0} C, lit[8]. mp 137.5 ^{0}C.

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