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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

HIO_3 in the Presence of Wet SiO_2: A Mild and Efficient Reagent for Selective Oxidation of Sulfides to Sulfoxides under Solvent-Free Conditions

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Published online: 20 Aug 2006.

To cite this article: M. M. Lakouraj, M. Tajbakhsh, F. Shirini & M. V. Asady Tamami (2005) HIO_3 in the Presence of Wet SiO_2: A Mild and Efficient Reagent for Selective Oxidation of Sulfides to Sulfoxides under Solvent-Free Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:6, 775-784, DOI: 10.1081/SCC-200050940

To link to this article: http://dx.doi.org/10.1081/SCC-200050940

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Synthetic Communications®, 35: 775–784, 2005

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1081/SCC-200050940

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Abstract: In the presence of wet SiO_2, HIO_3 is highly efficient for the selective oxidation of sulfides to sulfoxides. It may be applied to any type of dialkyl and alkyl aryl sulfides. It develops under solvent-free conditions, and gives high yield in the presence of different functional groups on the sulfide at room temperature.

Keywords: HIO_3/wet SiO_2, selective oxidation, solvent-free, sulfide, sulfoxide

Organic sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically significant molecules.[1] To date the synthesis of sulfoxides from sulfides has been widely explored and numerous oxidation procedures have been developed in an effort to achieve

Received in the U.K. June 10, 2004

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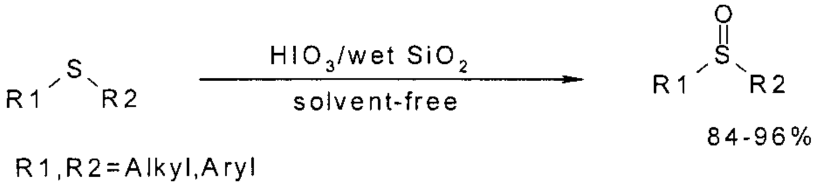
a facile, efficient, cheap, and selective method.[2] There are several reagents available for this conversion.[3] However, most reagents need carefully controlled reaction conditions, including the quantity of oxidants, because of the formation of sulfone as a side product.[4] Despite a number of alternative methods available for the synthesis of sulfoxides, oxidation of sulfides is the most favored method.[5]

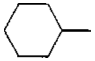
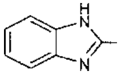
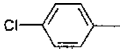
Popularity of this method is due to the availability of a wide variety of sulfides that can be utilized in such reaction. However, some of the oxidation procedures suffer from poor selectivity.[6] Unfortunately one or more equivalents, often hazardous or toxic oxidizing agents, and inert atmosphere or microwave assistance are usually required. Otherwise over-oxidation of sulfide, which results in sulfone formation and undesired reactions of other functional groups, are common problems.[7] As a consequence, the introduction of new, simple, less expensive, and safer methods and/or further work on technical improvements to overcome these limitations are still important experimental challenges.[8] Along this, recently much attention has been paid to methods and reactions that are performed either in solid phase or in the absence of solvents.[9] These reactions are of interest from different points of views and have developed into useful techniques for a variety of applications in organic chemistry, especially the solventless reactions conducted on solid supports.[10] Recently, we have reported HIO_3 as a mild, inexpensive, and efficient reagent for the coupling of thiols, and the convenient regeneration of carbonyls from oximes and hydrazones.[11] In the course of our study on oxidation of sulfides,[12] we herein explore the utility of this reagent for selective oxidation of sulfides to sulfoxide in the presence of wet SiO_2 under solvent-free conditions (Scheme 1). This reagent is readily prepared by adding HIO_3 to wet SiO_2, which is stable and could be stored for months without any activity lost at room temperature. This storable and easily handled reagent allows the conversion of sulfides to sulfoxides in mild conditions. These reactions share the virtues of ease of operation, simplicity of product isolation, formation of products in high yields, and the absence of side reactions including over-oxidation.

As shown in Table 1, a wide variety of sulfides are easily oxidized to the corresponding sulfoxides in high yields. The oxidation of methyl phenyl sulfide as the model compound was examined under solvent-free conditions



Scheme 1.

Table 1. Oxidation of sulfides to sulfoxides by HIO_3/wet SiO_2 under solvent-free condition[a]

Entry	R_1	R_2	Time (min)	Sulfoxide[b] (%)	Mp or bp (°C) found	Mp or bp (°C) reported(ref)
1	Ph	Me	50	95	30–32	33–34[13]
2	$PhCH_2-$	$PhCH_2-$	170	92	132–134	133–135[13]
3	n-Pr	n-Pr	2	87	73–75.1	75.05[14]
4	n-Bu	n-Bu	15	89	29–31.6	32.6[15]
5[c]	Ph	$PhCH_2$	170	93	123	117–121[14]
6	n-Oct	n-Oct	80	91	74–75	71–72[13]
7	$-CH_2CH_2CH_2CH_2-$		1	86	102–105	105–107[16] (12 mmHg)
8[c]	$4-MeC_6H_4$	$PhCH_2$	140	92	134–135	135–136[17]
9	Me	$-CH_2CH_2CHO$	1	84	oil	—
10	Ph	$-CH_2CH_2OH$	80	85	147–150.2	150–152.2[18]
11	$4-MeC_6H_4$	$-CH_2COOH$	90	86	106–109	—
12		$PhCH_2$	205	89	oil	oil[19]
13		Me	295	84	200–206	—
14[c]		$-CH_2CN$	275	85	69–73	—
15[c]	Ph	$-CH_2CH{=}CH_2$	25	86	—	$_{0.3}$85[20]
16	$-CH_2CH_2$ O CH_2 CH_2-		2	85	43–45	46–47.2[21]

[a] Reactions are carried out at room temperature using substrate/oxidant (1:3).

[b] Yields of isolated pure products.

[c] Reaction are carried out in a steam bath (45–50 °C).

at room temperature. The optimum ratio of sulfide to oxidant (1:3) is found to be ideal for complete conversion of sulfides to sulfoxides. Results show no sulfone formation in this reaction. By using this oxidation system, a variety of alkyl aryl, dialkyl, and diaryl sulfides were transformed to their corresponding sulfoxides. This solid-phase procedure is also applicable to long-chain aliphatic sulfides, which are normally insoluble in polar solvent and are therefore difficult to obtain by conventional methods (Table 1, entry 6). The selectivity of this procedure is remarkable toward sulfides. As evident from the results presented in the Table 1, chemoselective oxidation of sulfides to the corresponding sulfoxides has been achieved in the presence of a variety of functional groups, including alcohol, ether, alkene, aldehyde, and nitrile. In all the above experiments only sulfoxides were formed with no oxidation of other functional groups. Oxidation of 2-thiophenyl ethanol (Table 1, entry 10) to the corresponding sufoxide without any interference of oxidation of alcohol is notable, and allyl phenyl sulfide (Table 1, entry 15) afforded allyl phenyl sulfoxide in excellent yield without any complication from oxidation of carbon–carbon double bond.

To test the effectiveness of SiO_2, a model run was carried out with methyl phenyl sulfide in the absence of wet SiO_2 and we found that no sulfoxidation reactions took place within typical reaction time.

To show the strong and weak points of our method, we have compared the results of oxidation of methyl phenyl sulfide by our method with some of those reported in the literature under solvent-free conditions (Table 2). As indicated in Table 2, this method gives higher yield in shorter reaction time at ambient temperature without microwave assistance.

In conclusion, we have found a new and selective oxidation reaction of sulfides to sulfoxides with HIO_3 in the presence of wet SiO_2 that has many desirable features commending its use as an oxidantion method. This method offers the following advantages: a) the procedure is highly efficient and occurs under solvent-free conditions, b) the yield of sulfoxide is high, c) the reagent is cheap, safe, and easily prepared, and d) the selectivity of

Table 2. Comparison of our method with some of those reported in the literature[22(a,b,c,d)]

Reagent (condition)	Yield (%)/time (min)
$MnO_2/H_2SO_4/SiO_2$/Neat (1:2)[22a]	80/60
$Fe(NO_3)_3 \cdot 9H_2O$/Neat (1:2)[22b]	92/75
$NaIO_4/SiO_2$/MW (1:1.7)[22c]	80/2
$PhI(OAc)_2$/Alumina/MW (1:65:1.5)[22d]	82/0.75
Clayfen/MW[22e]	90/0.25
HIO_3/Wet SiO_2 (1:3)	95/50

this method is remarkable with regard to sulfides. Summing up, its high chemoselectivity together with features mentioned above makes this method a good alternative for conversion of sulfides to sulfoxides.

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka, and Aldrich chemical companies. All sulfides were prepared using the standard synthetic method.[23] Products were separated and purified by different chromatographic techniques and were also identified by the comparison of their mp, IR, NMR, and bp with those reported for the authentic samples. 1H NMR spectra were recorded on JNM-EX 90A or Bruker-DRX MH_2 NMR spectrometers.

General Procedure

To a mixture of HIO_3 (0.528 g, 3 mmol) and wet SiO_2 [(SiO_2/H_2O; 20% ww), 0.24 g] was added sulfide (1 mmol). The resulting mixture was stirred with a magnate bar at a room temperature or on a steam bath for the definite time (Table 1). The reaction was monitored by TLC (silica gelpolygram SiLG/UV 254 plates). After completion of the reaction, diethyl ether (5 ml) and sodium thiosulfate solution were added to the mixture and the resultant mixture was filtered after 15 min. Anhydrous Na_2SO_4 was added to the filtrate and filtered. Evaporation of the solvent gave the corresponding sulfoxides in good to high yields.

Products 1 to 16 are known compounds and their identities are established by comparison of their ^{1}HNMR and IR spectra with the data reported in the literature.[1,8,24–28]

Methyl Phenyl Sulfoxide (1)

^{1}HNMR: $\delta = 2.70$ (3H, s), 7.35–7.71 (5H, m).

IR (film): $\nu = 1050, 1093, 1406, 1450, 2920, 3070$m cm^{-1}.

Dibenzyl Sulfoxide (2)

^{1}HNMR: $\delta = 3.85$ (4H, s), 7.10–7.40 (10H, m).

IR (film): $\nu = 1035, 1080, 1410, 1450, 1500, 2960, 3025, 3070$, cm^{-1}.

Dipropyl Sulfoxide (3)

^{1}HNMR: $\delta = 1.08$ (6H, t), 1.85 (4H, sext), 2.50–2.74 (4H, m).

Dibutyl Sulfoxide (4)

^{1}HNMR: $\delta = 0.99$ (6H, t), 1.19–1.82 (8H, m), 2.70 (4H, t).

IR (film): $\nu = 1015, 1272, 1400, 1450, 2887, 2950, 2980,\ \text{cm}^{-1}$.

Benzyl Phenyl Sulfoxide (5)

^{1}HNMR: $\delta = 3.97$ (1H, d), 4.07 (1H, d), 6.88–7.00 (2H, m), 7.2–7.37 (3H, m), 7.38–7.50 (5H, m).

IR (film): $\nu = 696, 753, 1042, 1086, 1447, 1500, 2914, 2972, 3064,\ \text{cm}^{-1}$.

Diocthyl Sulfoxide (6)

^{1}HNMR: $\delta = 0.89$ (6H, t), 1.08–2.05 (24H, m), 2.67 (4H, t).

IR (film): $\nu = 993, 1014, 1082, 1461, 2900, 2910,\ \text{cm}^{-1}$.

Tetrahydrothiophen Oxide (7)

^{1}HNMR: $\delta = 1.80$–2.50 (4H, m), 2.55–2.90 (4H, m).

IR (film): $\nu = 1028, 1225, 1236, 1618, 1775, 1735, 2887, 2952,\ \text{cm}^{-1}$.

Benzyl (4-Methyl Phenyl) Sulfoxide (8)

^{1}HNMR: $\delta = 2.38$ (3H, s), 3.78–4.20 (2H, m), 7.52–7.45 (5H, m), 7.8 (4H, m).

3-(Methyl Sulfinyl) Propanal (9)

^{1}HNMR: $\delta = 2.51$ (3H, s), 2.84 (2H, m), 2.94–3.18 (2H, m), 10.16 (1H, s).

IR (film): $\nu = 970, 1045, 1148, 1210, 1620, 1742, 2620, 2960,\ \text{cm}^{-1}$.

2-(Phenyl Sulfinyl)-1-Ethanol (10)

^{1}HNMR: $\delta = 2.98$–3.2 (2H, m) 3.4 (1H, s), 3.9–4.3 (2H, m), 7.42–7.89 (5H, m).

IR (film): $\nu = 745, 990, 1033, 1429, 1610, 2869, 3726,\ \text{cm}^{-1}$.

2-[(4-Methyl Phenyl) Sulfinyl] Acetic Acid (11)

^{1}HNMR: $\delta = 2.4$ (3H, s), 3.84–3.95 (2H, s), 7.25–7.96 (4H, m), 9.98 (1H, s).

IR (film): $\nu = 885, 1016, 1049, 1093, 1236, 1271, 1398, 1488, 1627, 1703, 1745, 2559, 2999, 3449, cm^{-1}$.

MS (EI): m/z = 198, 181, 165, 162, 160, 148, 139, 128, 107, 91, 67, 62, 40.

Benzyl Cyclohexyl Sulfoxide (12)

^{1}HNMR: $\delta = 1.52-1.60$ (6H, m), 2.57 (1H, s), 2.87–2.95 (4H, m), 3.78–4.25 (2H, q), 7.22–7.48 (5H, m).

IR (film): $\nu = 698, 789, 892, 921, 922, 966, 1028, 1070, 1116, 1157, 1265, 1359, 1452, 1496, 1602, 2931, 3085, 3438, cm^{-1}$.

1-H-1,3-Benzimidazol-2-yl Methyl Sulfoxide (13)

^{1}HNMR: $\delta = 2.85$ (3H, s), 7.02–7.75 (4H, m), 10.4 (1H, s).

IR (film): $\nu = 738, 882, 964, 1014, 1099, 1147, 1220, 1267, 1317, 1359, 1440, 1498, 1589, 1618, 2385, 2686, 2923, 3053, cm^{-1}$.

MS (EI): m/z = 180, 165, 150, 132, 131, 118, 104, 90, 91, 62, 38.

[(4-Chloro Phenyl) Sulfinyl] Methyl Cyanide (14)

^{1}HNMR: $\delta = 3.53-3.64$ (2H, s), 7.36, 7.95 (4H, m).

IR (film): $\nu = 636, 742, 821, 1012, 1097, 1394, 1475, 1573, 2113, 2248, 2976, cm^{-1}$.

MS (EI): m/z = 185, 183, 173, 161, 159, 145, 111, 108, 99, 91, 81, 74, 67, 47, 46.

1-Allylsulfinylbenzene (15)

^{1}HNMR: $\delta = 3.55$ (2H, m, CH_2), 5.1 (1H, d, CH, J = 15 Hz), 5.32 (1H, d, CH, J = 11 Hz), 5.65 (1H, m, CH), 7.55 (5H, m).

IR: ν_{max} (neat)/$cm^{-1} = 1044$.

4-Oxo-1,4-Thioxane (16)

^{1}HNMR: $\delta = 2.40-3.10$ (m, 4H), 3.50–4.50 (m, 4H).

IR: $\nu-1025$, 1038, 1081, 1124, 1234, 1289, 1398, 1409, 1485, 1665, 2871, 2936, 2980.

ACKNOWLEDGMENT

We greatly acknowledge the research councils of Mazandran University for their financial support.

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