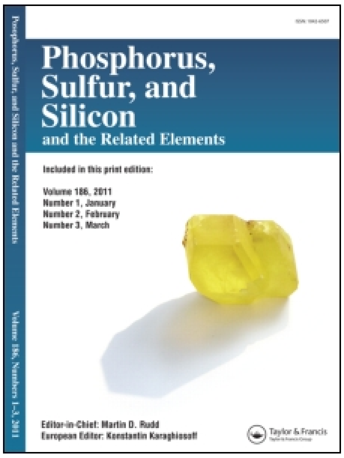

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Poly(Ethylene) Glycol as a Green and Reusable Solvent in the Oxidation of Sulfides to Sulfoxides Using NaClO

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POLY(ETHYLENE) GLYCOL AS A GREEN AND REUSABLE SOLVENT IN THE OXIDATION OF SULFIDES TO SULFOXIDES USING NaClO

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This article describes selective oxidation of a range of sulfides to the corresponding sulfoxides in good yields by NaClO in poly(ethylene) glycol as a green and reusable solvent using sulfuric acid as an efficient acid catalyst. The new method compares favorably with previous methods in literature. A separable mixture of two new diastereoisomers is reported.

Keywords Oxidation; poly(ethylene) glycol; sulfides, sulfoxides

INTRODUCTION

The search for new reaction media to replace volatile and often toxic solvents that are used in organic synthetic procedures is an important objective of significant environmental consequence. While the use of water as solvent is probably the most desirable approach, this is often not possible due to the hydrophobic nature of the reactants and the sensitivity of many catalysts to aqueous conditions. In this article, we describe the use of a widely available polymer, poly(ethylene) glycol (PEG 400), as nontoxic, inexpensive, and nonvolatile solvent for the oxidation of sulfides to sulfoxides.

Organic sulfoxides are excellent synthons for a vast variety of transformations in organic chemistry, such as C—C bond formation,[1] molecular rearrangement, and the preparation of biologically and medically important compounds.[2] The first oxidation of sulfides to sulfoxides was first described by Marker in 1865 using nitric acid.[3]

Recently, oxidation sulfides to sulfoxides via various catalysts and oxidants, such as Mn(III) complex,[4] VO(acac)$_2$,[5] cis-[MoO$_2$(phox)$_2$]/UHP,[6] immobilized cerium alkyl phosphonate,[7] *o*-iodoxybenzoic acid,[8] chromium(VI) oxide,[9] TaCl$_5$,[10] Ce(IV) triflate,[11] peroxotungstate immobilizedon ionic liquid–modified silica,[12] nitrophenyl-substituted polyperoxotungstate catalyst,[13] $NaBO_3.4H_2O$ or $Na_2CO_3.3H_2O_2$/SSA/KBr,[14] and tetrameric titanium alkoxide/ionic liquid,[15] are reported. Although a great number of new methods are available for the conversion of sulfides to corresponding sulfoxides, different kinds of drawbacks for those methods include use of metallic compounds, complex catalysts, or reagents; the formation of sulfones as side products; and a longer reaction time commonly required.

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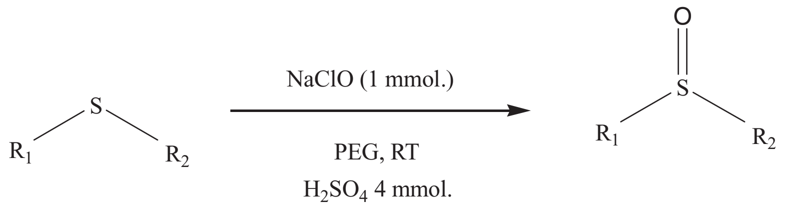
Therefore, there still is a need for the development of new methods for this transformation, as well as concern about all the above important protocols under the mild reaction condition.

It is further known that hypochlorous acid oxidation of certain sulfides leads to corresponding sulfoxides,[16] most probably via the corresponding chlorosulfonium ion as demonstrated by Johnson and McCants[17] in the oxidation of thianes with *tert*-butyl hypochlorite.[1c]c These types of oxidations are very much pH- and solvent-dependent, which also limits their use.

RESULTS AND DISCUSSION

In continuation of our work on safe and environmentally friendly procedures for preparation of chemical compounds,[18] we decided to look at the use of poly(ethylene) glycol as a reusable, inexpensive, nonvolatile, and commercially available solvent for the selective oxidation of sulfides to sulfoxides. We used NaClO and H_2SO_4 as cheap and commercially available reagents. The use of these cheap reagents and the environmentally benign nature of PEG encouraged us to couple them together and study their utility for oxidation of sulfides to sulfoxides.

To the best of our knowledge, there is no report in the literature on the selective oxidation of sulfides to sulfoxides under these conditions. Oxidation of sulfides was performed at room temperature in the presence of 4 mmol of sulfuric acid as catalyst and NaClO (1 mmol) 5.84% w/v as the oxidant in 4 mL polyethylene glycol as the solvent (Scheme 1).



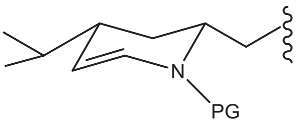
Scheme 1 Selective oxidation of sulfides to sulfoxides by NaClO in the presence sulfuric acid in poly(ethylene) glycol as solvent.

In a typical general experimental procedure, a solution of sulfide and NaClO (both 1 mmol) in 4 mL of PEG in the presence of sulfuric acid (4 mmol) was stirred for 45–70 min, resulting in the formation of the corresponding sulfoxides without any over oxidation and with good to excellent yields. To study the scope of this procedure, a series of various substituted sulfides including alkyl aryl sulfides and dialkyl sulfides was reacted according to optimized reaction conditions. The results are summarized in Table I.

The process is devoid of sulfone formation, a byproduct common to most other peroxide-based oxidations even by warming the reaction mixture to 50 °C. It is important to note that some alpha hydroxyl phenylthio compounds, which have been successfully oxidized by this reagent in other solvents such as water and EtOH/water,[18e,f] did not work in these conditions.

In order to investigate the recyclability of poly(ethylene) glycol (it is immiscible with ether), the oxidation product was extracted with it and the retained PEG phase was reused. The solvent phase was recycled with a decrease in reactivity for three cycles, and an approximately 5% weight loss of PEG was observed from each cycle.

Table I Oxidation of sulfides to sulfoxides using NaClO in poly(ethylene) glycol/H_2SO_4 at room temperature

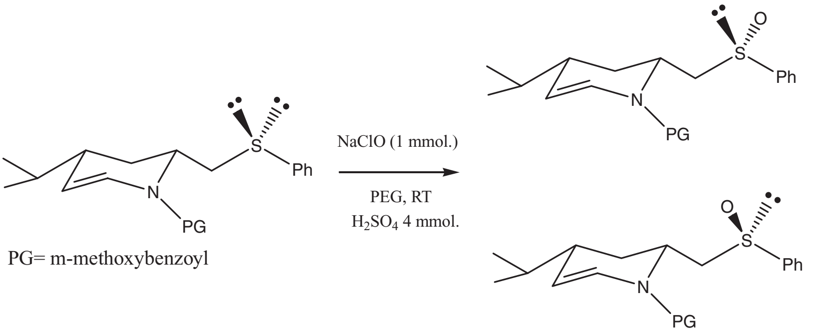
Entry	R_1	R_2	Time (min)	Yield (%)[a] with H_2SO_4 as catalyst
1	Ph	Me	55	75
2	Ph	Et	45	80
3	Ph	Ph	60	85
4	Ph	Bn	70	90
5	Et	Et	60	80
6	Et	Me	65	72
7	n-Pr	n-Pr	70	75
8	n-Bu	n-Bu	60	78
9[b]	Ph	 PG= m-methoxybenzoyl	70	85[c]

[a] Isolated yield.

[b] The starting material was prepared according to ref. no. [19].

[c] Two diastereoisomers were separated.

It is interesting to note (see Table I) that for protected 2-phenylthio dehydropiperidine derivative (entry 9), two possible diastereoisomers were observed (Scheme 2). Note that the sulfur atom is chiral.[19] Based on the literature,[20, 21] and based on our recent work,[18e, f] as there is no neighboring hydroxyl group to assist, both of sulfur's electron pairs are available, and the results are logical. Two mentioned diastereoisomers can be separated by flash chromatography and characterized by spectroscopic methods (Scheme 2). The ^{1}H NMR spectrum shows clearly the difference between the two diastereoisomers. The less polar diastereoisomer gives a triplet at 4.85 ppm integrating for one proton and corresponding to the axial proton of C-6, and the corresponding peak for the more polar diatereoisomer is a triplet at 4.75 ppm. The geminal protons of the phenylsulfinylmethyl for the less polar diastereoisomer appear at 3.25 and 3.15 ppm in the form of doublets of doublets, while the corresponding signals for more polar diastereoisomer appear at 3.40 and 3.20 ppm.



Scheme 2 Two possible diastereoisomers for oxidation of protected 2-phenylthio dehydropiperidine.

The less polar diastereoisomer has an R_f value of 0.39 (Et.:Hex., 90:10), and the most polar diastereoisomer has an R_f value of 0.25 (Et.:Hex., 90:10).

In conclusion, a fast and exclusive generation of various sulfoxides from the corresponding sulfides was achieved using NaClO in polyethylene glycol as solvent in the presence of H_2SO_4 as catalyst at room temperature. The reaction is highly selective and efficient. The use of a reusable solvent, the exceptionally fast reaction rate, the absence of a need for control of temperature, and no formation of over-oxidized products make this protocol an attractive alternative to the existing methodologies.

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer, model 783 spectrophotometer. The NMR spectra have been recorded by a Bruker AMX-300 (300 MHz) spectrometer. The chemical shifts are expressed in parts per million (ppm), and tetramethylsilane (TMS) was used as internal reference. The mass spectra (MS) were recorded on an AEI MS-902 model.

General Procedure

A solution of sulfide (1 mmol) and diluted NaClO (1 mmol, 1.25 mL) (5.84% w/v) in poly(ethylene) glycol (4 mL), and sulfuric acid (4 mmol) was stirred vigorously for an appropriate time (45–70 min). After completion of the reaction (monitored by TLC), the reaction mixture was cooled in a dry ice/acetone bath to precipitate the PEG 400 and organic products extracted with ether. The ether layer was washed with water (2 mL) and dried over $MgSO_4$. The organic solvent was removed under reduced pressure to give the corresponding pure sulfoxide (Table I). Two sulfoxides from entry 9 ($R_f = 0.39$; diethyl ether:hexane, 90:10) and ($R_f = 0.25$; diethyl ether:hexane, 90:10) were separated and purified by flash chromatography as oily products. The recovered PEG 400 can be reused for three runs.

Known compounds were identified by IR and ^{1}H NMR spectral data.

3-Isopropyl-5-phenylsulfinylmethyl-1,2-dehydro Piperidine

Less polar diastereoisomer. R_f: 0.39 (Et.:Hex., 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, J = 8 and 2 Hz, 1H), 7.50 (m, 3H), 7.30 (t, J = 7 Hz, 1H), 7.00 (m, 3H), 6.50 (d, J = 6 Hz, 1H), 5.05 (m, 1H), 4.85 (t, J = 4 Hz, 1H), 3.82 (s, 3H), 3.25 (dd, J = 7 and 3 Hz, 1H), 3.15 (dd, J = 7 and 4 Hz, 1H), 2.20 (m, 1H), 2.10 (m, 1H), 1.85 (m, 1H), 1.65 (m, 1H) and 1.00 (dd, J = 9 and 6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 159.5, 144.4, 136.0, 131.1, 129.4, 129.3, 124.1, 119.2, 116.3, 113.3, 112.1, 61.9, 55.4, 47.9, 37.9, 32.7, 30.2 and 20.3. IR (neat): 3062, 2958, 2861, 1717, 1639, 1439, 1361, 1253, 1046, 749, 691 and 633 cm^{-1}. MS (m/e): 398 (MH$^+$); Calculated: 398.17899; Obtained: 398.17790.

More polar diastereoisomer. R_f: 0.25 (Et.:Hex., 90:10). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, J = 8 and 2 Hz, 1H), 7.50 (m, 3H), 7.30 (t, J = 7 Hz, 1H), 7.00 (m, 3H), 6.50 (d, J = 6 Hz, 1H), 5.10 (dd, J = 6 and 2 Hz, 1H), 4.75 (t, J = 4 Hz, 1H), 3.83 (s, 3H), 3.40 (dd, J = 7 and 3 Hz, 1H), 3.20 (dd, J = 7 and 4 Hz, 1H), 2.23 (m, 1H), 2.10 (m, 1H), 1.85 (m, 1H), 1.65 (m, 1H) and 1.00 (dd, J = 9 and 5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 159.5, 144.4, 136.0, 131.1, 129.4, 129.3, 124.1, 119.2, 116.3, 113.3, 112.1, 61.9, 55.4, 47.9, 37.9, 32.1, 30.2 and 20.3. IR (neat): 3060, 2955, 2860, 1715, 1640, 1440, 1360, 1250, 1045, 750, 690 and 630 cm^{-1}. MS (m/e): 398 (MH$^+$); Calculated: 398.17899; Obtained: 398.17830.

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