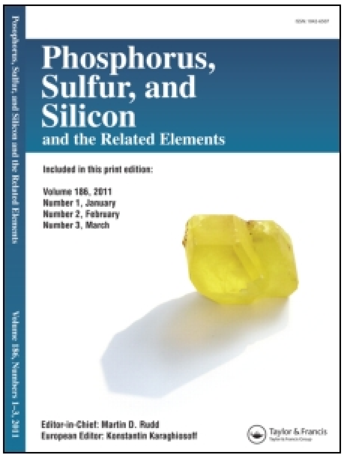

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Fast and Efficient Oxidation of Sulfides to Sulfones With *N,N*'-Dibenzyl-*N,N,N*',*N*'-Tetramethyl Diammonium Permanganate

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To cite this Article Lakouraj, M. M. , Tajbakhsh, M. , Tashakkorian, H. and Ghodrati, K.(2007) 'Fast and Efficient Oxidation of Sulfides to Sulfones With *N,N*'-Dibenzyl-*N,N,N*',*N*'-Tetramethyl Diammonium Permanganate', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 2, 485 — 490

To link to this Article: DOI: 10.1080/10426500600977338

URL: http://dx.doi.org/10.1080/10426500600977338

Phosphorus, Sulfur, and Silicon, 182:485–490, 2007
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600977338

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Fast and Efficient Oxidation of Sulfides to Sulfones With *N,N′*-Dibenzyl-*N,N,N′,N′*-Tetramethyl Diammonium Permanganate

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Selective oxidation of sulfides to sulfones was developed using N,N′-dibenzyl-N,N,N′,N′-tetramethylethylene diammonium permanganate. A variety of aromatic and aliphatic sulfides were oxidized to the corresponding sulfones immediately in excellent yields at r.t.

Keywords Diammonium permanganate; selective oxidation; sulfide; sulfone

INTRODUCTION

Sulfur derivatives have been studied extensively as useful precursors for pharmaceutically, biologically, and chemically important compounds due to their extensive use in modern synthetic chemistry.[1–4] Recently, sulfones have been employed for stabilizing α–radicals[5] and α-anions,[6] and they have been used as cationic synthons.[7] A variety of methods have been reported for the oxidation of sulfides to sulfones in the literature.[8–17]

Conversions of sulfides to sulfones under both homogeneous[18,19] and heterogeneous[20] conditions have been well described. Among them, a few permanganate-based reagents such as methyltriphenylphosphonium permanganate,[21] tetra-*n*-butylammonium permanganate,[22] and benzyltriethylammonium permanganate[23] have been developed. These ammonium permanganates are unstable and must be used freshly prepared or with essential caution in handling and storage. For these

Received May 1, 2006; accepted July 26, 2006.

We are grateful to the Research Councils of Mazandaran University, Babolsar, Iran, for their financial support.

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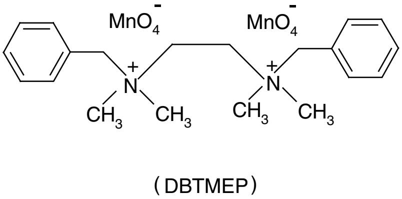


SCHEME 1

reasons, there is still need for a stable reagent that is capable of carrying out such transformations fast and efficiently. In continuation of our previous work on oxidation of sulfides[24,25] and thiols,[26] we introduce a new, efficient, and fast reagent for this purpose. We prepared *N,N′*-Dibenzyl-*N,N,N′,N′*-Tetramethyl Diammonium Permanganate (DBTMEP) as a bench-top reagent (Scheme 1), which is thermally stable up to 110°C and efficient for the selective oxidation of sulfides to sulfones.

RESULTS AND DISCUSSION

DBTMEP was prepared on treatment of *N,N′*-dibenzyl-*N,N,N′,N′*-tetramethyl diammonium bromide with a freshly prepared aqueous permanganate solution by a simple ion-exchange reaction. This reagent is a purple powder, is nonhygroscopic, and can be stored in dark glass vessels for months without any loss of activity.

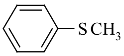
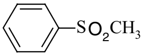
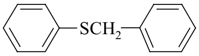
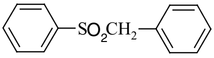
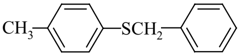
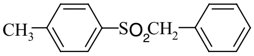
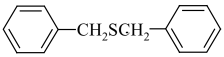
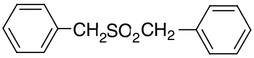
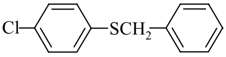
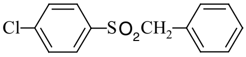
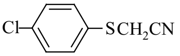
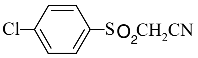
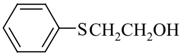
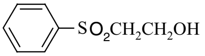
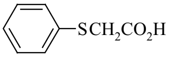
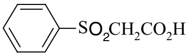
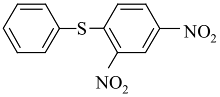
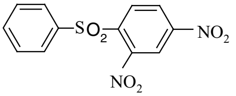
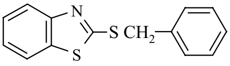
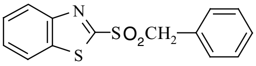
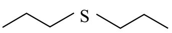
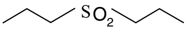
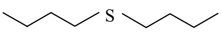
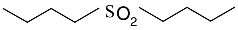
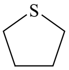
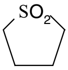
In order to find the optimum reaction conditions, we tried to oxidize phenyl methyl sulfide as a model compound with our reagent at r.t. First, the oxidation reactions were carried out in different solvents in order to explore the effect of the solvent. The results are shown in Table I.

As indicated in Table I, oxidation in organic solvents, such as *n*-hexane, dichloromethane, and acetonitrile, needs a long reaction time. However the addition of a small amount of acetic acid or using acetic

TABLE I Effect of Solvent on Reaction Conversion

Solvent	Time (h)	Yield (%)
n-Hexane	48	20
CH_2Cl_2	36	25
CH_3CN	24	40
AcOH	<2 min	97
AcOH/H_2O(1:1)	<2 min	97
CH_3CN/AcOH(8:1)	<2 min	97

TABLE II Oxidation of Sulfides to Sulfones by DBTMEP at R.T.[a]

Substrate	Product[b]	Yield (%)[c]	M.P. (Lit.)[32]
		97	85(85–87)
		97	147 (148)
		96	146 (144–145)
		95	149 (150)
		93	122–123
		92	168 (169)
		95	121.5 (120)
		95	113 (111.5–112.5)
		93	156 (157)
		92	99 (—)
		95	31 (29–30)
		95	45 (46–46.5)
		92	27 (25–28)

[a] Reactions were completed within 2 min in methanol.

[b] All products were identified by comparing the IR, NMR, and TLC data with those of authentic samples.

[c] Yields refer to isolated product.

acid as the solvent shows a significant effect on reaction time and completes the reaction immediately. The $CH_3CN/AcOH$ ratio of 8:1 gave the best result, and the optimum sulfide/reagent ratio was found to be 1:1 for this conversion.

To show the general applicability of this method, we have treated different aromatic sulfides with DBTMEP at r.t. in $CH_3CN/AcOH$. The results are presented in Table II. As indicated in Table II, selective

TABLE III Comparison of DBTMEP With Other Reagents Reported in the Literature for the Oxidation of Sulfides to Sulfones

Substrate	Reagents/Conditions/Time	Yields (%)	Ref.
PhSMe	Caro's acid/SiO_2/CH_3CN, reflux/4.5 h	92	24
PhSMe	TBAO/Im/Mn(TPP)OAc	96	27
PhSMe	Oxone/CH_2Cl_2, r.t./2 h	98	15
PhSMe	Na_2WO_4-$C_6H_5PO_3$-PTC/50°C, 30%H_2O_2/2 h	97	14
PhSMe	30%H_2O_2, $NaHCO_3$, Mn Catalyst/ DMF, r.t./0.25 h	85	28
PhSMe	30%H_2O_2, $NaHCO_3$, Mn Catalyst/ CH_3CN, r.t./0.25 h	93	28
PhSMe	30%H_2O_2, $NaHCO_3$, Mn Catalyst/ r.t./0.25 h.	70	28
PhSMe	**DBTEMP/r.t., CH_3CN-CH_3CO_2H**	**97**	
(*n*-Butyl)$_2$S	Caro's acid/SiO_2/CH_3CN, reflux/4.5 h	84	24
(*n*-Butyl)$_2$S	Na_2WO_4-$C_6H_5PO_3$-PTC/50°C, 30%H_2O_2/1 h.	95	14
(*n*-Butyl)$_2$S	H_2O_2-CH_3CN/0°C, MeOH/12 h	90	29
(*n*-Butyl)$_2$S	Oxone/CH_2Cl_2, r.t./2 h	94	15
(*n*-Butyl)$_2$S	$KMnO_4$-$CuSO_4$/CH_2Cl_2, reflux/25 h	98	20
(*n*-Butyl)$_2$S	H_2O_2-CF_3COOH/0°C, CF_3COOH	80	17
(*n*-Butyl)$_2$S	30%H_2O_2/$ArSeO_2H$/CH_2Cl_2/3 h	100	30
(*n*-Butyl)$_2$S	**DBTEMP/r.t., CH_3CN-CH_3CO_2H**	**95**	

oxidation of sulfides to the corresponding sulfones is achieved at ambient temperature. Aliphatic sulfides as well as aromatic ones were oxidized immediately at r.t. in excellent yields (Table II). Functional groups including hydroxyl and cyano groups were unaffected under these reaction conditions.

In order to show the advantages and drawbacks of our method, we have compared some of our results with those reported in the literature.[14,15,17,20,24,27–30]

As indicated in Table III, DBTMEP oxidized sulfides to sulfones immediately at r.t. without the need of any catalyst. In conclusion, we have prepared and introduced DBTMEP as a new, fast, and efficient reagent for the conversion of sulfides to sulfones in excellent yields. Its high stability, selectivity, and excellent reaction yields can make the present oxidation method a useful addition to the existing procedures.

EXPERIMENTAL

Chemicals were purchased from Merck (Germany), Fluka (Switzerland), and Aldrich (UK) chemical companies. A number of sulfides were prepared using the standard synthetic method.[31] All sulfones were separated and purified by different chromatographic techniques and also identified by the comparison of their m.p., b.p., IR, and NMR data with those of authentic samples reported in literature.[32] ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 90 NMR spectrometer with tetramethylsilane as an internal reference and $CDCl_3$ as the solvent. IR spectra were recorded on a Pye-Unicam SP 1100 spectrophotometer.

Preparation of DBTMEP

To the mixture of *N,N′*-tetramethylethylene diamine (1 mol) in DMF (10 mL), benzyl bromide (2.5 mol) was added dropwise at 60°C. After stirring for 1 h at this temperature, the white precipitate was filtered off and washed with ether (5 mL). The diammonium salt (1 mol) was dissolved in water and poured slowly into a fresh, saturated aqueous potassium permanganate solution (3 mol) at ambient temperature. A purple precipitate was formed, which was collected by filtration and washed with water to remove the excess of permanganate (yield: 95%). Care must be taken because DBTMEP decomposes violently when subjected to harsh grinding. ^{1}H NMR(acetone-d_6): $\delta = 3.35$ (s, 12H, CH_3), 4.45 (s, 4H, CH_2), 4.85 (s, 4H, CH_2), 7.55 7.95 (m, 10H, arom. H). ^{13}C NMR(acetone-d_6): $\delta = 49.5$, 55.2, 69.2, 125.7, 129.2, 131.5, 132.6. IR (KBr) ν (cm^{-1}): 3469, 3393, 3021, 2967, 1485, 1464, 1216, 996, 892, 865, 741.

General Procedure for Conversion of Sulfides to the Corresponding Sulfones Using DBTMEP

To the solution of sulfide (1 mmol) in CH_3CN (4 mL) and acetic acid (0.5 mL), DBTMEP (536 mg, 1 mmol) was added in portions within 2 min. The mixture was stirred at r.t. during the addition. Monitoring by TLC (*n*-hexane/ethylacetate 18/2) showed completion of the reaction immediately after addition of the reagent. On completion, the solvent was evaporated, NaOH (10%, 10 mL) was added to the residue, and the product was extracted with diethyl ether (2 × 15 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure to afford the corresponding pure sulfone in an excellent yield.

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