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Oxidation of sulfides to sulfoxides and sulfones with 30% hydrogen peroxide under organic solvent- and halogen-free conditions

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In honor of Professor Henri B. Kagan on the occasion of his award of the prestigious Tetrahedron Prize

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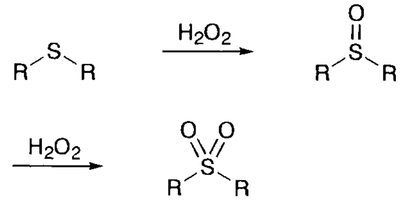
Abstract—Aromatic and aliphatic sulfides are oxidized to sulfoxides or sulfones in high yield with 30% hydrogen peroxide under organic solvent- and halogen-free conditions. Dialkyl and alkyl aryl sulfides are cleanly oxidized to sulfoxides using aqueous hydrogen peroxide without catalysts. The best catalyst for the sulfone synthesis consists of sodium tungstate, phenylphosphonic acid, and methyltrioctylammonium hydrogensulfate. Co-existing primary or secondary alcohol or olefinic moieties are unaffected under such conditions. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides and sulfones,[1] both of which are important as commodity chemicals and, in some cases, as pharmaceuticals.[2] Conventional oxidants include, among others, $NaBO_3$,[3] NaClO,[4] $Ca(ClO)_2$,[5] $H_5IO_6/[Mn^{IV}\text{–}Mn^{IV}\text{-}(\mu\text{-}O)_3L_2](PF_6)_2$,[6] $KHSO_5$,[7,8] HNO_3,[9] $(NH_4)_2Ce(NO_3)_6$,[10] $NaIO_4$,[11,12] MnO_2,[13] $KMnO_4$,[14] RuO_4,[15] CF_3CO_3H,[16] dimethyldioxirane,[17,18] $t\text{-}C_4H_9O_2H$,[19] 4-methylmorpholine oxide with OsO_4,[20] $3\text{-}ClC_6H_4CO_3H$,[21] and $[(n\text{-}C_4H_9)_4N]HSO_5$.[22,23] Unfortunately, most of these reagents are not satisfactory for medium- to large-scale synthesis because of the low content of effective oxygen, the formation of environmentally unfavorable co-products, and high cost. Singlet oxygen[24] or molecular oxygen combined with $CH_3CH(CH_3)CHO$[25] or $CH_3CH(CH_3)CH_2CHO$ and $Co(acac)_2$[26] has also been used. Aqueous hydrogen peroxide (H_2O_2) of <60% concentration is an ideal oxidant[27] in view of an effective-oxygen content of as high as 47%, cleanness that produces only harmless water by reaction, safety in storage and operation, and the low cost of production and transportation.[28] These obvious advantages have spurred the development of useful procedures for H_2O_2 oxidation of sulfides, including the use of various tungsten (W) catalyst systems such as H_2WO_4,[29] $[C_5H_5N(n\text{-}C_{16}H_{33})]_3PO_4\text{-}[W(O)(O_2)_2]_4$,[30] $Na_2WO_4+[(n\text{-}C_4H_9)_4N]Cl$,[31] $K_{12}WZnMn_2\text{-}(ZnW_9O_{34})_2+[CH_3(n\text{-}C_8H_{17})_3N]Cl$,[32] $[(n\text{-}C_4H_9)N](C_6H_5)_2\text{-}PO_2[W(O)(O_2)_2]_2$,[33] and $H_3PW_{12}O_{40}+[(n\text{-}C_8H_{17})_4N]Br$[34] were used in addition to CH_3ReO_3,[35] CH_3ReO_3,[36] $2\text{-}NO_2C_6H_4SeO_2H$,[37] $Na_2MoO_4+(n\text{-}C_4H_9)_3PO$,[38] and hemoglobin.[39] However, there remains much room for improvement, because many of these procedures require either chlorohydrocarbon solvents that affect human health and the environment,[30–33,35,37,38] or anhydrous H_2O_2 in ethanol.[36,40] We here describe an organic solvent- and halogen-free oxidation of sulfides using 30% H_2O_2.



(1)

2. Results and discussion

2.1. Oxidation to sulfones

First, we selected as a model diphenyl sulfide, a relatively unreactive substrate. The optimum conditions were searched by reaction using a diaryl sulfide (10 mmol) and 30% H_2O_2 (25 mmol) with various W catalysts (0.02 mmol; substrate/catalyst molar ratio, *S*/*C* of 500) and a quaternary ammonium salt (0.02 mmol) as a phase-transfer catalyst (PTC) without any organic solvents. The reactions were conducted at 25°C for 2 h with magnetic stirring at 1000 rpm. The results are summarized in Table 1. As noted earlier in olefin epoxidation,[41] oxidation of the sulfide

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Keywords: green chemistry; hydrogen peroxide; oxidation; phase-transfer catalyst; quaternary ammonium salts; sulfides; sulfones; sulfoxides.

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Table 1. Effects of catalysts on oxidation of diphenyl sulfide

Catalyst	PTC	Additive	pH_{init}[a]	% yield of sulfone[b]
–	–	–	4.8	0
–	–	$C_6H_5PO_3H_2$	1.4	0
–	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	–	1.1	0
$Na_2WO_4 \cdot 2H_2O$	–	–	4.8	0
	–	$C_6H_5PO_3H_2$	2.0	0
	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	–	2.4	13
	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	H_3PO_4	1.3	28
	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	$C_6H_5PO_3H_2$	1.8	72
	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	$NH_2CH_2PO_3H_2$	2.6	7
	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	$(C_6H_5)_2PO_2H$	1.8	2
	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	$(C_6H_5)_3PO$	4.6	11
	$[CH_3(n\text{-}C_8H_{17})_3N]Cl$	$C_6H_5PO_3H_2$	2.5	50
H_2WO_4	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	$C_6H_5PO_3H_2$	0.5	53
	$[CH_3(n\text{-}C_8H_{17})_3N]OH$	$C_6H_5PO_3H_2$	2.8	66
	$[CH_3(n\text{-}C_8H_{17})_3N]Cl$	$C_6H_5PO_3H_2$	0.8	49

Reaction was run using diphenyl sulfide (10 mmol), 30% H_2O_2 (25 mmol), catalyst (0.02 mmol), PTC (0.02 mmol), and additive (0.02 mmol) with stirring at 1000 rpm at 25°C for 2 h.

[a] Initial pH value of the aqueous layer after mixing the two phases.

[b] Determined by ^1H NMR analysis. Based on diphenyl sulfide charged.

was efficiently achieved in the presence of small amounts of Na_2WO_4, a phosphonic acid promoter, and an acidic quaternary ammonium salt, $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. The presence of both W catalyst and PTC is crucial. $C_6H_5PO_3H_2$ was the best promoter, giving diphenyl sulfone in 72% yield. Without the phosphonic acid under otherwise identical conditions, the yield was lowered to 13%. H_3PO_4, $NH_2CH_2PO_3H_2$ (best promoter for olefin epoxidation), and $(C_6H_5)_2PO_2H$ were less effective than $C_6H_5PO_3H_2$. The use of 30% H_2O_2 is recommended, while 60% H_2O_2 oxidizes the sulfide more rapidly. A reaction did not occur at 25°C when using 5% H_2O_2. Although this catalyst system is operationally the most convenient, Na-free systems using H_2WO_4 can also be used with equal success. A quaternary ammonium chloride having the same alkyl chains gave a somewhat lower yield. It should be added that the Freyermuth conditions using 30% H_2O_2, H_2WO_4, NaOH, and CH_3CO_2H ($S/C=250$, pH 5.6, 75°C, 2 h) convert 2-hydroxyethyl phenyl sulfide to the hydroxy sulfone in 95% yield[29] but are not applicable to the oxidation of diphenyl sulfide. We confirmed that this procedure does not oxidize the diaryl sulfide at all at 25°C (sulfide/H_2O_2=1:2.5, $S/C=250$, pH 6.0 or even 0.2, 2 h) and gives diphenyl sulfone only in 7% yield at 60°C.

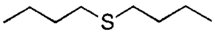
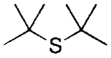
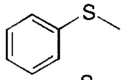
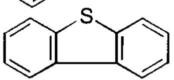
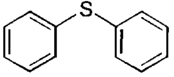
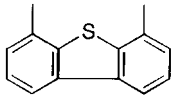
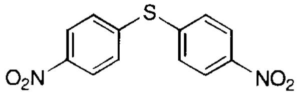
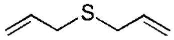
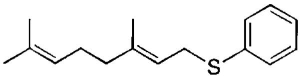
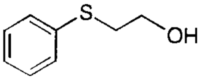
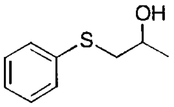
The reaction proceeds more rapidly at higher temperatures with lower catalyst loading, proving to be a useful synthetic procedure. Thus, when a mixture of diphenyl sulfide, 30% H_2O_2, $Na_2WO_4H_2O$, $C_6H_5PO_3H_2$, and $[CH_3(n\text{-}C_8H_{17})_3N]$-$HSO_4$ (substrate/H_2O_2/W/phosphonic acid/PTC=1000:2500:1:1 mol ratio, $S/C=1000$) placed in a round-bottomed flask was stirred at 50°C for 2 h at 1000 rpm, diphenyl sulfone was obtained in 99% yield. This catalytic reaction is highly productive. A turnover number (TON, mol product/mol W) as high as 122,000 was achieved in the oxidation using the diaryl sulfide, H_2O_2, W catalyst, $C_6H_5PO_3H_2$, and PTC in a ratio of 1,000,000:1,000,000:1:1:100 to produce the sulfone in 12.2% yield after 326 h at 50°C. This TON should be compared with the reported highest values 236 or 154 obtained with the more reactive alkyl aryl sulfides, $C_6H_5S(CH_2)_2OH$ (W catalyst)[29] and $C_6H_5SC_2H_5$ (Mo catalyst),[33] respectively, although these values could be improved by optimizing the conditions. A 100 g scale oxidation was conducted without problems under the aqueous/organic biphasic conditions to give the sulfone in 96% yield. The oxidation can be performed with hexane, toluene, or ethyl acetate as co-solvent, if necessary, for crystalline substrates. No chlorohydrocarbon solvents are required.

Table 2 lists some other examples of oxidation. The reaction using a small excess of 30% H_2O_2 proceeded smoothly with an S/C of 1000–5000 at 25–50°C. Yields were consistently high. It was found that both aromatic and aliphatic sulfides can be used, with the latter being more reactive. The electron withdrawing NO_2 group in the phenyl ring or bulky, even two tertiary alkyl substituents do not affect the synthetic efficiency. The chemoselectivity is noteworthy. Under such conditions, the sulfide function is highly reactive, and various other functional groups are tolerable. Diallyl sulfide was cleanly converted to diallyl sulfone without epoxidation. Normally reactive tri-substituted olefinic bonds[41] were also left intact. Primary and secondary alcohols[42] were unaffected. 2-Hydroxyethyl and -hydroxypropyl phenyl sulfide were oxidized to the sulfone products without dehydrogenation of the alcohol function.

2.2. Oxidation to sulfoxides

The oxidation of sulfides to sulfones obviously proceeds via the sulfoxide intermediates. The H_2O_2 oxidation to sulfoxides has a long history since 1908,[43,44] and it has frequently been used with[1e,45,46] or without catalysts[47–51] in various organic solvents. However, the scope and limitations have not been clarified in the literature. Although solvent- and catalyst-free oxidation is highly desirable, no standard protocols utilizing mere aqueous H_2O_2 have been established. The only reported example is for thiacyclopentane giving thiacyclopentane oxide.[52] We noted that, as expected, the susceptibility of sulfides to H_2O_2 is highly dependent on the substituents, as shown in Table 3. For selective oxidation of dialkyl sulfides to the sulfoxides, we recommend a simple procedure to treat a sulfide with an equimolar amount of 30% H_2O_2 at 35°C, as tested by a

Table 2. Hydrogen peroxide oxidation of sulfides to sulfones

Sulfide		H_2O_2 mmol (equiv.)	Na_2WO_4, $C_6H_5PO_3H_2$, and PTC, mmol (*S*/*C*)^{a}	Temp. (°C)	Time (h)	% yield of sulfone
Structure	mmol					
	10	25 (2.5)	0.01 (1000)	50	1	95^{b}
	10	25 (2.5)	0.01 (1000)	50	3	91^{b}
	10	25 (2.5)	0.01 (1000)	50	2	97^{c}
	10	25 (2.5)	0.01 (1000)	50	3	88^{d,e}, 97^{f,g}
	537^{h}	1343 (2.5)	0.54 (1000)	50	2	96^{i}
	53.7	134 (2.5)	0.05 (1000)	50	2	92^{i}, 99^{f}
	53.7	134 (2.5)	0.01 (5000)	50	18	87^{i}
	10	25 (2.5)	0.01 (1000)	50	24	90^{d,i}, 98^{d,f}
	10	25 (2.5)	0.01 (1000)	50	12	93^{f,j}
	10	25 (2.5)	0.01 (1000)	50	24	94^{e,j}
	10	25 (2.5)	0.01 (1000)	25	2	93^{c}
	10	25 (2.5)	0.005 (2000)	25	24	97^{c}
	10	25 (2.5)	0.01 (1000)	25	8	95^{c}
	10	25 (2.5)	0.01 (1000)	25	6	91^{c}
	10	25 (2.5)	0.005 (2000)	25	24	91^{c}
	10	25 (2.5)	0.01 (1000)	25	9	98^{c}

Unless otherwise stated, reaction was run using 30% H_2O_2. PTC=$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

[a] Substrate/catalysts molar ratio.

[b] Isolated by recrystallization from hexane.

[c] Isolated by silica-gel column chromatography.

[d] Toluene (10 mL) was used as solvent.

[e] Recrystallization from acetonitrile.

[f] Determined by ^{1}H NMR.

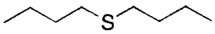
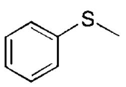
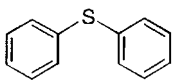
[g] Hexane (10 mL) was used as solvent.

[h] Added dropwise.

[i] Recrystallization from toluene.

[j] Ethyl acetate (20 mL) was used as solvent.

Table 3. Hydrogen peroxide oxidation of sulfides to sulfoxides

Sulfide	Na_2WO_4, $C_6H_5PO_3H_2$, and PTC, mmol (*S*/*C*)^{a}	H_2O_2 mmol (equiv)	Temp. (°C)	Time (h)	% Yield^{b}	
					Sulfoxide	Sulfone
	–	10 (1.0)	35	18	99	<1
	–	68.4 (1.0)^{c}	35	18	99^{d}	0
	–	11 (1.1)	0	9	31	0
	0.005 (2000)	11 (1.1)	0	9	93	7
	–	10 (1.0)	35	18	99	<1
	–	80.5 (1.0)^{c}	35	18	99^{d}	0
	–	11 (1.1)	0	9	39	0
	0.005 (2000)	11 (1.1)	0	9	94	6
	–	25 (2.5)	50	12	2	0
	0.005 (2000)	12 (1.2)	25	3	61	21

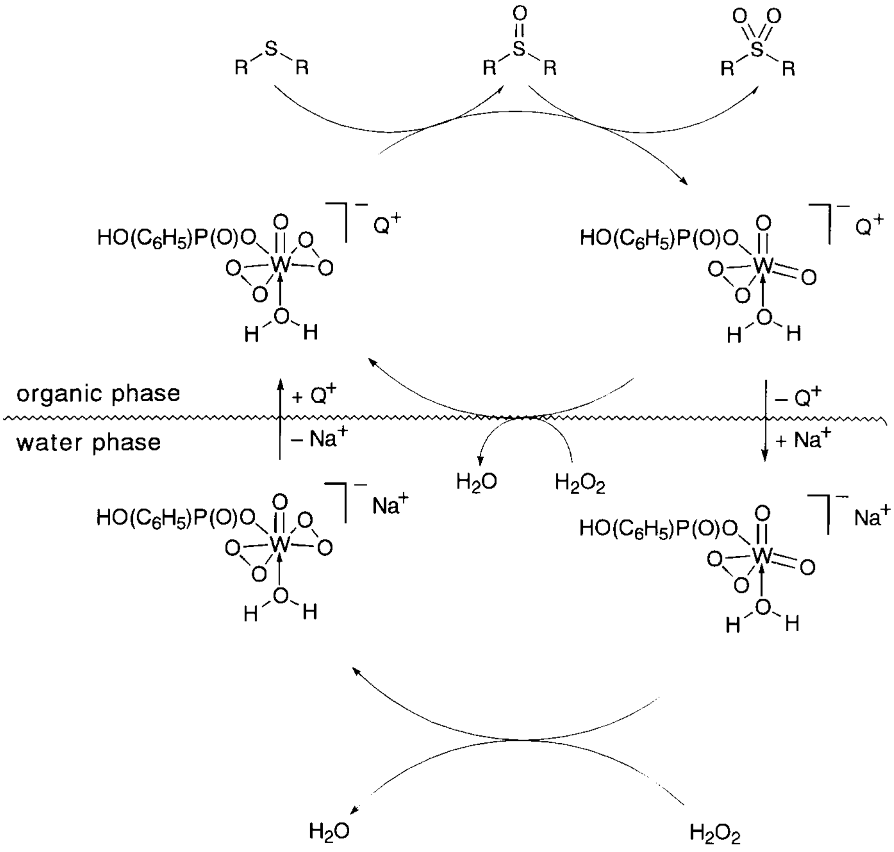
Unless otherwise stated, reaction was run using sulfide (10 mmol) and 30% H_2O_2. PTC=$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$.

[a] Substrate/catalysts molar ratio.

[b] Determined by ^{1}H NMR.

[c] Reaction was run with 10 g of sulfide.

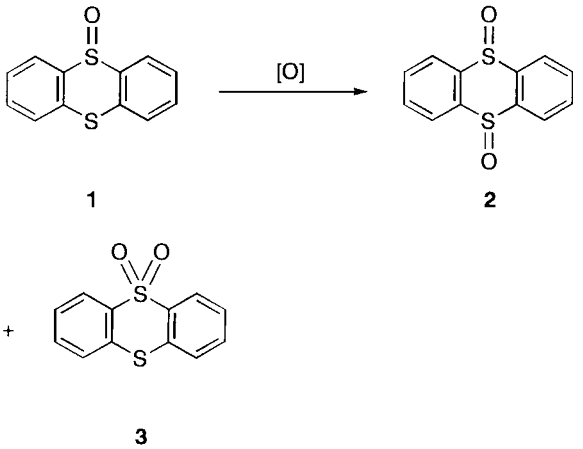
[d] Isolated yield.



Scheme 1. Proposed catalytic cycle. Q^+=quaternary ammonium ion.

10 g scale reaction of dibutyl sulfide. Neither organic solvent[47–51] nor metal catalyst[1e,45,46] is necessary. The second oxidation to dibutyl sulfone is very slow under such conditions. The oxidation below room temperature is slower, while raising the temperature to 50°C and with excess H_2O_2 forms an appreciable amount of the sulfone. In the presence of the W catalyst system consisting of Na_2WO_4, $C_6H_5PO_3H_2$, and PTC (*S*/*C*=2000), oxidation of dibutyl sulfide using 1.1 equiv. of 30% H_2O_2 occurs smoothly even at 0°C to give the sulfoxide in 93% yield (31% yield without catalyst). Methyl phenyl sulfide is somewhat less reactive than dibutyl sulfide but behaves similarly. However, diaryl sulfides are different. Diphenyl sulfide is almost inert to 30% H_2O_2 below 50°C in the absence of catalysts. The reaction using 1.2 equiv. of H_2O_2 and the W catalyst system at 25°C for 3 h gave diphenyl sulfoxide in 61% yield together with diphenyl sulfone in 21% yield. The use of 2.5 equiv. of H_2O_2 led cleanly to the sulfone, as described above. Separate experiments showed that both the first and second steps require the W catalyst, although $C_6H_5PO_3H_2$ is unnecessary in the sulfoxide-to-sulfone conversion.

It should be noted that, under the standard catalytic conditions using an equimolar amount of H_2O_2, the bifunctional substrate **1** was oxidized at the sulfide site to give **2** with >99:1 selectivity. This chemoselectivity is to be compared with those observed with H_2O_2/HCl, **2**:**3**=90:10,[53] and H_2O_2/NaOH, >1:99.[53] H_2O_2 oxidation of **1** with a CH_3ReO_3 catalyst is known to give a 38:62 mixture of **2** and **3**.[54]



1 **2** **3** (2)

2.3. Catalytic cycle

Although further scrutiny is necessary to identify the exact reactive species, we now consider that the catalytic oxidation takes place by the cycle of Scheme 1. The use of acidic hydrogensulfate ion in the PTC generates bis(peroxo)-tungsten mono-anion, while the lipophilic quaternary ammonium ion carries the oxidant efficiently to an organic phase.[42a] The ligation of phenylphosphate to the W center would increase the reactivity of the peroxo ligands. The electrophilicity of the peroxotungstate intermediates is much higher than that of H_2O_2. The reoxidation of the mono(peroxo)tungsten ion to the bis-peroxo species with H_2O_2 occurs either in the aqueous phase or the aqueous/organic interface, or even to some extent in the organic phase.[55] Unlike olefin epoxidation,[41] neighboring hydroxy groups do not accelerate the oxidation to a great extent. 2-Hydroxyethyl phenyl sulfide is oxidized only two times faster than methyl phenyl sulfide, while 2-hydroxyethyl phenyl sulfoxide and methyl phenyl sulfoxide are converted to sulfones at nearly equal rates.

3. Conclusion

This W catalyst system efficiently promotes the oxidation of aromatic and aliphatic sulfides with 30% H_2O_2 and a W catalyst under organic solvent- and halogen-free biphasic conditions. The oxidation is selective for sulfides or sulfoxides, leaving an olefinic linkage or alcoholic moiety intact. Overall, we recommend this simple, clean, and economical procedure for the oxidation of various sulfides on a medium to large scale.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were measured on a JEOL JNM-A400 NMR spectrometer at 400 and 100 MHz, respectively. The chemical shifts of ^1H NMR spectra are reported in ppm on δ scale downfield from tetramethylsilane, which was used as an internal standard, and the signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. The chemical shifts of ^{13}C NMR spectra are reported in ppm with chloroform-*d* (77.00 ppm) as an internal standard. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 H or JMS-700 mass spectrometer. Melting points were determined on a YANAKO MP-J3 apparatus and are uncorrected. High-performance liquid chromatographic (HPLC) analyses were performed on a Waters 2690 Separation Module with a Waters 486 Tunable Absorbance Detector using a Develosil ODS-5 column (4.6 mm×25 cm, NOMURA CHEMICAL).

4.2. Materials

$Na_2WO_4\cdot 2H_2O$, H_2WO_4, aqueous 30% H_2O_2, H_3PO_4, $C_6H_5PO_3H_2$, $(C_6H_5)_3PO$, bromobenzene, and thiophenol were obtained from Nacalai Tesque and were used as received. $(C_6H_5)_2PO_2H$ was obtained from Aldrich Chemical, and was used as received. Dibutyl sulfide, di-*t*-butyl sulfide, methyl phenyl sulfide, diphenyl sulfide, dibenzothiophene, di-*p*-nitrophenyl sulfide, diallyl sulfide, 2-hydroxyethyl phenyl sulfide, thianthrene, propylene oxide, geraniol, and $[CH_3(n\text{-}C_8H_{17})_3N]Cl$ were purchased from Tokyo Kasei Kogyo, and were used as received. Toluene, hexane, acetonitrile, and ethyl acetate were obtained from Nacalai Tesque and were distilled before use. $[CH_3(n\text{-}C_8H_{17})_3N]OH$ was prepared from $[CH_3(n\text{-}C_8H_{17})_3N]Cl$ using AMBERLITE IRA900 (ORGANO). $NH_2CH_2PO_3H_2$[56] and 4,6-dimethyldibenzothiophene[57] were synthesized according to the literature. 2-Hydroxypropyl phenyl sulfide was obtained from propylene oxide and sodium thiophenolate. Geranyl phenyl sulfide was prepared by the reaction of sodium thiophenolate and geranyl chloride, which was synthesized from geraniol and $(C_6H_5)_3P$ in CCl_4. Thianthrene 5-oxide and thianthrene 5,10-dioxide were obtained by the oxidation of thianthrene with 30% H_2O_2 in the presence of $Na_2WO_4\cdot 2H_2O$, $C_6H_5PO_3H_2$, and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. Thianthrene 5,5-dioxide was synthesized by the oxidation of thianthrene 5-oxide with basic H_2O_2 in methanol.

4.2.1. 2-Hydroxypropyl phenyl sulfide.[58] Bp 95.0–95.5°C/0.5 mm Hg. ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, 3H, J=6.4 Hz), 2.68 (br, 1H), 2.85 (dd, 1H, J=4.8, 13.6 Hz), 3.07 (dd, 1H, J=4.0, 13.6 Hz), 3.82–3.87 (m, 1H), 7.17–7.21 (m, 1H), 7.25–7.29 (m, 2H). 7.35–7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.83, 43.31, 65.52, 126.42, 128.91, 129.84, 135.22.

4.2.2. Geranyl phenyl sulfide.[59] Bp 90.0–91.0°C/0.2 mm Hg. ^1H NMR (400 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.59 (s, 3H), 1.67 (s, 3H), 1.97–2.05 (m, 4H), 3.54 (d, 2H, J=7.6 Hz), 5.04–5.07 (m, 1H), 5.29–5.33 (m, 1H), 7.15–7.33 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.00, 17.66, 25.64, 26.42, 32.16, 39.54, 119.22, 123.89, 125.96, 128.65, 129.85, 131.62, 136.75, 139.85.

4.2.3. Thianthrene 5-oxide.[60] Mp 149.0–150.0°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (dt, 2H, J=1.2, 7.6 Hz), 7.56 (dt, 2H, J=1.2, 7.6 Hz), 7.64 (dd, 2H, J=1.2, 7.6 Hz), 7.94 (dd, 2H, J=1.2, 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.49, 128.43, 128.45, 129.01, 129.84, 141.43.

4.2.4. Thianthrene 5,5-dioxide.[60] Mp 169.0–170.0°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.56 (m, 4H), 7.66–7.68 (m, 2H), 8.21–8.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.46, 127.70, 128.72, 132.01, 135.10, 135.30.

4.2.5. Thianthrene 5,10-dioxide.[60] Mp 279.0–280.0°C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70–7.75 (m, 4H), 8.05–8.10 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.69, 130.77, 138.34.

4.3. Preparation of methyltrioctylammonium hydrogensulfate

A 1 L, one-necked, round-bottomed flask equipped with a magnetic stirring bar was charged with 4.186 g of $[CH_3(n\text{-}C_8H_{17})_3N]Cl$ (10.34 mmol), 200 g of 49% H_2SO_4 (1.02 mol), and 200 mL of toluene. The biphasic mixture was vigorously stirred at room temperature for 12 h. The aqueous phase was removed, and 200 g of 49% H_2SO_4 (1.02 mol) was added to the organic phase and vigorously stirred at room temperature for 12 h. The organic phase was separated, dried over anhydrous Na_2SO_4 for 24 h, and filtered. Removal of volatile material in vacuo gave 4.840 g (99%) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as a white solid. No detectable amount of Cl^- was observed by aqueous $AgNO_3$ titration. $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ can also be prepared by our previously reported method.[41b]

4.4. Procedure for the oxidation of diphenyl sulfide: general procedure for the 100 g scale oxidation

A 500 mL, four-necked, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a 100 mL dropping funnel was charged with 177 mg (0.537 mmol) of $Na_2WO_4 \cdot 2H_2O$, 250 mg (0.537 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 85 mg (0.537 mmol) of $C_6H_5PO_3H_2$, and 152 g (1343 mmol) of aqueous 30% H_2O_2, and the mixture was vigorously stirred at room temperature for 10 min. With vigorous stirring, 100 g (537 mmol) of diphenyl sulfide was added dropwise via the dropping funnel over a period of 1 h, while maintaining the temperature of the reaction mixture below 50°C. The mixture was stirred for an additional 1 h at 50°C, then cooled to room temperature. The white precipitate was separated by filtration and washed with 50 mL of cold water. The product was recrystallized from toluene giving 112.8 g (96%) of diphenyl sulfone as white crystals, mp 128.0–129.0°C.

4.5. Procedure for oxidation of diallyl sulfide: general procedure for the 10 mmol scale oxidation

A 20 mL flask was charged with 3.3 mg (0.01 mmol) of $Na_2WO_4 \cdot 2H_2O$, 4.7 mg (0.01 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 1.6 mg (0.01 mmol) of $C_6H_5PO_3H_2$, and 2.83 g (25 mmol) of aqueous 30% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 1.14 g (10 mmol) of diallyl sulfide was added. This mixture was stirred at 25°C at 1000 rpm for 2 h. The organic phase was separated, washed with 10 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (silica gel 60, 80 g; eluent, 4:1 hexane/ethyl acetate) to give 1.36 g (93%) of diallyl sulfone as a colorless liquid.

4.6. Procedure for oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide without catalyst: general procedure for the 10 g scale oxidation

A 100 mL flask was charged with 10.0 g (80.5 mmol) of methyl phenyl sulfide and 9.13 g (80.5 mmol) of aqueous 30% H_2O_2, and the mixture was stirred at 35°C at 1000 rpm for 18 h. The resulting homogeneous solution was saturated with NaCl and extracted with ethyl acetate (3×20 mL). The organic phase was washed with 20 mL of saturated aqueous $Na_2S_2O_3$, dried over Na_2SO_4, and concentrated under reduced pressure to give 11.2 g (99%) of methyl phenyl sulfoxide as white crystals, mp 30.0–30.5°C.

4.7. Procedure for determining the turnover number of the catalytic oxidation

A 500 mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 177 μg (1 M solution in water, 0.537 μL, 0.537 μmol) of $Na_2WO_4 \cdot 2H_2O$, 25.0 mg (1 M solution in methanol, 53.7 μL, 53.7 μmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 84.9 μg (1 M solution in water, 0.537 μL, 0.537 μmol) of $C_6H_5PO_3H_2$, and the solvent was removed under vacuum. To this was added 152 g (1.34 mol) of aqueous 30% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 100 g (0.537 mol) of diphenyl sulfide and 8.55 g (54.4 mmol) of bromobenzene as internal standard were added. This mixture was heated at 50°C for 326 h with stirring at 1000 rpm. The yield of diphenyl sulfone was determined to be 12.2% by HPLC analysis of small aliquots of the organic phase. The HPLC data were corrected for the relative response of the detector by integrating the response of each analyte against bromobenzene. HPLC (column, Develosil ODS-5, 4.6 mm× 25 cm, NOMURA CHEMICAL); eluent, 1:1 water–CH_3CN mixture; flow rate, 0.75 mL/min; detection, 254 nm light; retention time (t_R) of diphenyl sulfoxide, 8.5 min; t_R of diphenyl sulfone, 13.6 min; bromobenzene (internal standard), 27.9 min; t_R of diphenyl sulfide, 54.5 min.

4.7.1. Chemoselective oxidation of thianthrene 5-oxide. A 20 mL, round-bottomed flask equipped with a magnetic stirring bar was charged with 0.825 mg (0.1 M solution in water, 25 μL, 2.5 μmol) of $Na_2WO_4\ 2H_2O$, 1.16 mg (0.1 M solution in methanol, 25 μL, 2.5 μmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 0.395 mg (0.1 M solution in water, 25 μL, 2.5 μmol) of $C_6H_5PO_3H_2$. After the solvent was removed under vacuum, 567 mg (5 mmol) of aqueous 30% H_2O_2 and 1 mL of ethyl acetate were added. The mixture was vigorously stirred at room temperature for 10 min, then 110.7 mg (0.477 mmol) of thianthrene 5-oxide and 71.7 mg (0.457 mmol) of bromobenzene as internal standard were added. This mixture was stirred at 1000 rpm at 25°C for 7 min. The yields of thianthrene 5,5-dioxide and thianthrene 5,10-dioxide were determined by HPLC analysis to be <0.1 and 23%, respectively. The HPLC data were corrected by integrating the response of each analyte against bromobenzene. HPLC (column, Develosil ODS-5, 4.6 mm×25 cm, NOMURA CHEMICAL); eluent, 1:1 water–CH_3CN mixture (0–15 min) then CH_3CN; flow rate, 0.5 mL/min; detection, 254 nm light; t_R of thianthrene 5,10-dioxide, 11.5 min; t_R of thianthrene 5-oxide, 23.9 min; bromobenzene (internal standard), 28.3 min; t_R of thianthrene 5,5-dioxide, 35.4 min.

4.7.2. Dibutyl sulfone.[61] Mp 46.0–46.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, 6H, J=7.4 Hz), 1.44–1.53 (m, 4H), 1.78–1.86 (m, 4H), 2.93–2.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.53, 21.78, 23.93, 52.46.

4.7.3. Di-*t*-butyl sulfone.[36] Mp 130.0–131.0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.05, 64.75.

4.7.4. Methyl phenyl sulfone. Mp 89.0–90.0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 3H), 7.56–7.60 (m, 2H), 7.65–7.69 (m, 1H), 7.95–7.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.67, 127.32, 129.34, 133.67, 140.58. HRMS (FAB$^+$) m/z Calcd for $C_7H_8NaO_2S$ ($[M+Na]^+$): 179.0143. Found: 179.0148.

4.7.5. Dibenzothiophene-5,5-dioxide. Mp 232.0–232.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, 2H, J=1.2, 7.2 Hz), 7.65 (dt, 2H, J=1.2, 7.2 Hz), 7.80–7.85 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.55, 122.20, 130.38, 131.62, 133.86, 137.74. HRMS (FAB$^+$) m/z Calcd for $C_{12}H_8NaO_2S$ ($[M+Na]^+$): 239.0143. Found: 239.0154.

4.7.6. Diphenyl sulfone.[62] Mp 128.0–129.0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.59 (m, 6H), 7.94–7.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.65, 129.26, 133.15, 141.61.

4.7.7. 4,6-Dimethyldibenzothiophene-5,5-dioxide. Mp 244.0–244.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 6H), 7.24 (d, 2H, J=7.6 Hz), 7.47 (t, 2H, J=7.6 Hz), 7.57 (d, 2H, J=7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.85, 118.75, 131.89, 132.06, 133.39, 135.68, 135.71. HRMS (EI^+) m/z Calcd for $C_{14}H_{12}O_2S$ (M^+): 244.0558. Found: 244.0556.

4.7.8. Di-*p*-nitrophenyl sulfone.[62] Mp 271.0–271.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.19 (m, 4H), 8.38–8.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.88, 129.43, 145.76, 150.89.

4.7.9. Diallyl sulfone.[63] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (d, 4H, J=7.6 Hz), 5.45 (dd, 2H, J=1.2, 16.8 Hz), 5.52 (dd, 2H, J=1.2, 10.4 Hz), 5.93 (tdd, 2H, J=7.6, 10.4, 16.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.92, 124.79, 124.83.

4.7.10. 2-Hydroxyethyl phenyl sulfone.[64] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (br, 1H), 3.35 (t, 2H, J=5.2 Hz), 4.01 (t, 2H, J=5.2 Hz), 7.60 (t, 2H, J=7.6 Hz), 7.68–7.72 (m, 1H), 7.95 (d, 2H, J=7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.33, 58.24, 127.95, 129.47, 134.07, 138.94.

4.7.11. 2-Hydroxypropyl phenyl sulfone. Mp 44.0–46.0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, 3H, J=6.4 Hz), 3.16–3.29 (m, 2H), 3.46 (s, 1H), 4.30–4.36 (m, 1H), 7.58–7.62 (m, 2H), 7.67–7.71 (m, 1H). 7.92–7.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.52, 62.27, 63.27, 127.81, 129.39, 133.99, 139.10. HRMS (FAB^+) m/z Calcd for $C_9H_{12}NaO_3S$ ($[M+Na]^+$): 223.0405. Found: 223.0415.

4.7.12. Geranyl phenyl sulfone.[65] Mp 43.0–45.0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.58 (s, 3H), 1.68 (s, 3H), 2.00 (s, 4H), 3.80 (d, 2H, J=8.0 Hz), 5.02 (m, 1H), 5.18 (t, 1H, J=8.0 Hz) 7.51–7.55 (m, 2H), 7.61–7.65 (m, 1H). 7.85–7.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.13, 17.65, 25.66, 26.17, 39.65, 56.08, 110.28, 123.41, 128.55, 128.91, 132.06, 133.49, 138.64, 146.36.

4.7.13. Dibutyl sulfoxide.[66] Mp 34.0–34.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, 6H, J=7.4 Hz), 1.41–1.57 (m, 4H), 1.72–1.79 (m, 4H), 2.60–2.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.64, 22.05, 24.56, 52.13.

4.7.14. Methyl phenyl sulfoxide.[67] Mp 30.0–30.5°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73 (s, 3H), 7.48–7.56 (m, 3H), 7.64–7.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.95, 123.47, 129.33, 131.00, 145.72.

4.7.15. Diphenyl sulfoxide.[62] Mp 72.0–73.0°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.49 (m, 6H), 7.63–7.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.77, 129.30, 131.03, 145.61.

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