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Cerium (IV) triflate-catalyzed selective oxidation of sulfides to sulfoxides with aqueous hydrogen peroxide

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ABSTRACT

Cerium (IV) triflate catalyzes the selective oxidation of a variety of dialkyl, alkyl aryl and cyclic sulfides to the corresponding sulfoxides in the presence of aqueous hydrogen peroxide (50%) in high yields. The method is compatible with many functional groups including alcohols, aldehydes, olefins, halogens, nitriles and esters.

1. Introduction

The selective oxidation of sulfides to sulfoxides is an important transformation because of the importance of the latter as an intermediate in organic synthesis [1] and the key role it plays in the enzyme activation [2]. Although several methods for the selective oxidation of sulfides to sulfoxides have been developed [3–5], very few are sufficiently selective to terminate oxidation at the sulfoxide stage [2,6–14]. Hypervalent iodine reagents might be a good choice for the oxidation of sulfides to sulfoxides, but insolubility and compatibility of these reagents with commonly used solvents and the need to employ halogenated solvents are major drawbacks [7,15,16]. There are a number of oxygen donors in the literature, but the use of H_2O_2, O_2, and ^tBuOOH have become increasingly more important in the green context [17–19]. Among these, aqueous H_2O_2 is the most attractive as it shows safety in storage and operation, is commercially available and relatively cheap [20]. Moreover, aqueous hydrogen peroxide is a waste-avoiding oxidant, since water is the only byproduct. It is also a very attractive oxidant for liquid-phase reactions because of its solubility in water and many organic solvents [21,22]. Various transition metal (Ti, Mo, Fe, V, W, Re, Ru, Mn, Zr, and Sc) compounds have been used as activators of hydrogen peroxide [23–27,9].

Lanthanides are gaining increasing importance in the field of organic synthesis [28,29]. Cerium salt has long been used for the oxidation of alcohols [30–33], hydroquinones [34], hydrazines [35] and sulfides [36–40]. Ceric ammonium nitrate (CAN), used in conjunction with CH_3CN–H_2O [36], molecular oxygen [38,40], and $NaBrO_3$ [37], has been used to oxidize sulfides to sulfoxides. But ceric ammonium nitrate catalyzed reactions take long time and are not equally good for all kind of substrates. As an example, oxidation with CAN in CH_3CN–H_2O is restricted to diaryl sulfides [36]. This method is not suitable for dialkyl sulfides having α-hydrogen. Although CAN-mediated oxidation with molecular oxygen [38,40] is a green process, it suffers drawbacks. The reaction is slow and reactions need to be heated to 60–100 °C. The reaction also requires a high pressure of oxygen. Recently, Sullivan and coworkers reported that immobilized cerium alkyl phosphonate in the presence of sodium bromate can oxidize sulfides to sulfoxides [41]. The reaction gives good selectivity but is very slow and need to be heated to 40–80 °C. Although commercial cerium (IV) triflate [42–47] has already been used as a Lewis acid catalyst in nitrone cycloaddition, protection/deprotection, epoxide ring-opening and esterification reactions, its use in oxidation has not been studied extensively. In this paper, the use of $Ce(OTf)_4$ as a catalyst for the selective oxidation of sulfides to sulfoxides, mediated by aqueous hydrogen peroxide (50%) in tetrahydrofuran, is reported.

2. Results and discussion

In continuation of our interest in sulfur chemistry [8,48,49], we were in search of a high-yielding, catalytic, cheap and environmentally benign reagent for sulfide oxidation and considered $Ce(OTf)_4{\cdot}xH_2O$–H_2O_2 as a reagent of choice. Thus when phenyl

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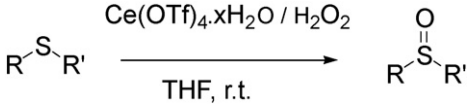


Scheme 1. Synthesis of sulfoxide.

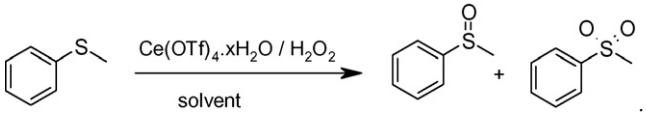
methyl sulfide was treated with $Ce(OTf)_4{\cdot}xH_2O$ and 50% aqueous H_2O_2 in THF, phenyl methyl sulfoxide was obtained in 93% isolated yield. The general reaction is shown in Scheme 1.

Considering methyl phenyl sulfide as a model substrate, it was subjected to different reaction conditions as shown in Table 1. The oxidation was investigated in various solvents such as toluene, THF, CH_3CN, CH_3NO_2, CH_3OH, CH_3COOH and CH_2Cl_2 using 1 mol% of catalyst. The efficiency of toluene and THF as a solvent was found to be similar with a minimum amount of sulfone formation. The drawback of toluene is that some of the substrates are not completely soluble in this solvent. The reaction also proceeded in CH_3CN, CH_3NO_2, and CH_3COOH but with the formation of more sulfone, while in methanol, almost equal amounts of sulfoxide and sulfone were formed. There was no reaction in CH_2Cl_2. Therefore, THF is proved to be the optimum solvent and was used in subsequent optimization studies. At a lower concentration of hydrogen peroxide (2 equiv.), the reaction took a longer time (60 min) and produced 7% of sulfone. Increasing the amount of hydrogen peroxide to 4 and 5 equiv. decreased the time (30 min), but also increased the amount of sulfone to 13 and 20%, respectively. With 3 equiv. of H_2O_2, the over-oxidation to sulfone was minimized (3%). The reaction was also performed with mixed solvent system such as THF/toluene (1:1) and 2 equiv. of H_2O_2, but it took longer time (3 h) and produced more sulfone (6%).

The reaction was also monitored with different catalyst loadings. At a lower catalyst loading (0.1 mol%) the reaction took longer time and was not complete even after stirring for 4 h, while with 0.5 mol% catalyst, the reaction was completed in 2 h, yielding 97% sulfoxide with a small amount of sulfone (3% yield). It was also observed that by increasing the amount of catalyst to 5 mol%, the reaction led to more sulfone (15%) along with unreacted sulfide (6%). The oxidation reaction was also carried out with $CeCl_3{\cdot}7H_2O$ in tetrahydrofuran. It was observed that the reaction proceeded with this catalyst but with a low selectivity and longer time (Table 2). Therefore, an optimum amount of catalyst and oxidant with a suitable solvent for the above oxidation is necessary and based on the above observation we come to a conclusion that 1 mol% of $Ce(OTf)_4$, 3 equiv. of 50% H_2O_2 and THF as a solvent is the best combination for oxidation of sulfides to sulfoxides with good selectivity. It was also found that without H_2O_2, $Ce(OTf)_4{\cdot}xH_2O$ alone cannot oxidize sulfides to sulfoxides.

A wide range of sulfides was subjected to oxidation with very high selectivity and excellent yields being observed in all cases (Table 3). It was observed that sulfides, irrespective of the presence of electron-withdrawing or -releasing groups, were oxidized equally well to sulfoxides. For example compound having highly electron-withdrawing groups (entries 8 and 9) and electron-releasing groups (entries 15 and 16) gave almost the same yield. This is only possible if the reaction proceeds via single electron transfer because the radical, once formed, is stabilized both by electron-withdrawing and -releasing groups. Since the presence of an electron-withdrawing group reduces the sulfides to be oxidized to the radical cation (as shown in mechanism), substrates having electron-withdrawing groups took more time for oxidation. It is worth noting that sulfides in entries 7, 8, 18 and 19 (electron-withdrawing groups) react comparatively slowly. The

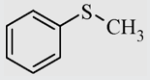
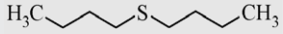
Table 1
Oxidation of methyl phenyl sulfide at different conditions



Solvent	H_2O_2[a] (equiv.)	Time (min)	Sulfoxide (% yield)[b]	Sulfone (% yield)[b]
Toluene	3	60	97	3
THF	2	60	93	7
	3	40	97	3
	4	30	87	13
	5	30	80	20
	2	360	94	6
CH_3CN	3	30	89	11
CH_3NO_2	3	30	92	8
CH_3OH	3	30	53	47
CH_3COOH	3	30	76	24
CH_2Cl_2	3	60[c]	0	0

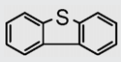
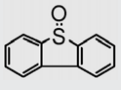
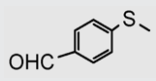
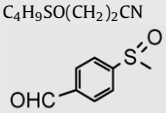
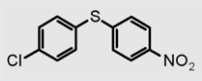
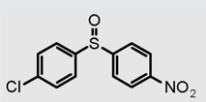
[a] 50% H_2O_2 was used.
[b] Determined by GC–MS and ^1H NMR.
[c] Continued for 12 h.

Table 2
Oxidation of sulfides to sulfoxides catalyzed by $CeCl_3{\cdot}7H_2O$.

Entry	Substrates	Time (h)	Sulfoxide (yield)[a]	Sulfone (yield)[a]
1		48	71	29
2		46	78	22

[a] Determined by ^1H NMR.

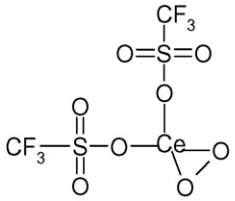
Table 3
Oxidation of sulfide into sulfoxide.

Entry	Substrate (**a**)	Time (h)	Product (**b**)	Yield[a,b] (%)
1	$PhSCH_3$	0.7	$PhSOCH_3$	93(97)
2	$PhSC_6H_{13}$	3	$PhSOC_6H_{13}$	96(97)
3	$PhSCH_2CO_2C_2H$	6	$PhSOCH_2CO_2C_2H_5$	93(98)
4	$PhS(CH_2)_4OAc$	5	$PhSO(CH_2)_4OAc$	94(96)
5	$PhCH_2S(CH_2)_2OH$	3	$PhCH_2SO(CH_2)_2OH$	95(96)
6	$C5H_{11}S(CH_2)_2OH$	3	$C5H_{11}S(CH_2)_2OH$	95(96)
7	$p\text{-}BrC_6H_4SC_2H_5$	10	$p\text{-}BrC_6H_4SOC_2H_5$	92(97)
8	$PhSCFCl_2$	11	$PhSOCFCl_2$	91(95)
9	$PhSCH_2CH_2CN$	6	$PhSOCH_2CH_2CN$	95(98)
10	$PhSCH_2Ph$	6	$PhSOCH_2Ph$	94(97)
11	$PhSCH_2CH{=}CH$	6	$PhSOCH_2CH{=}CH_2$	92(95)
12	$PhCH_2SCH_2Ph$	6	$PhCH_2SOCH_2Ph$	93(97)
13		13		91(95)
14	$C_{16}H_3{}_3SC_6H_{13}$	5	$C_{16}H_{33}SOC_6H_{13}$	89(94)
15	$C_{12}H_{25}SC_6H_{13}$	4	$C_{12}H_{25}SOC_6H_{13}$	94(94)
16	$C_4H_9SC_4H_9$	0.5	$C_4H_9SOC_4H_9$	91(95)
17	$C_4H_9S(CH_2)_2CN$	2	$C_4H_9SO(CH_2)_2CN$	92(97)
18		12		90(97)
19		65		73(78)

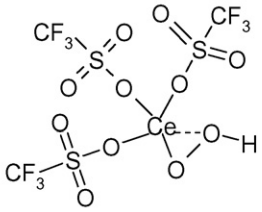
[a] Isolated yields.
[b] Yield in the parenthesis is on the basis of ^1H NMR.

reaction is extremely mild and equally good for alkyl aryl, dialkyl and cyclic sulfides. The method proved to be compatible with many functional groups like alcohol, aldehyde, olefin, halogen, nitrile and ester. Many oxidizable substrates like alcohol (entries 5 and 6), olefin (entry 11) and aldehyde (entry 18) and hydrolyzable substrates such as cyanides (entries 9 and 17) and esters (entries 3 and 4) remain intact under these reactions conditions. Interestingly dichlorofluoromethyl phenyl sulfide (entry 8) having three-electron-withdrawing groups directly attached to the sulfur atom gives very good yield. Cyclic sulfide (entry 13) is also efficiently sulfoxidated. Unfortunately this reagent system is not suitable for the oxidation of sulfides to sulfones as it requires longer time, oxidant as well as catalyst.

The mechanism of the reaction is not clear. The formation of peroxo **A** or hydroperoxide **B** species may be possible, which could be responsible for the rate acceleration and chemoselectivity of the reaction.



A



B

3. Conclusion

In conclusion, a highly selective and highly active catalyst for the oxidation of sulfides to sulfoxides has been achieved under mild conditions. Under these reaction conditions, functional groups such as hydroxyl, acetate, ester, olefin, halogen and nitrile remain unaffected. As both catalyst and oxidant are environmentally benign reagents this protocol may be considered as a green approach for the selective oxidation of sulfides into sulfoxides.

4. Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker DRX-300 (300 MHz) and Varian AS 400 (400 MHz) spectrometer using TMS as internal standard. IR spectra were recorded on Nicolet Impact 410 FT-IR spectrometer.

4.1. Typical procedure for the oxidation of sulfide into sulfoxide

A mixture of methyl phenyl sulfide (124 mg, 1.0 mmol), $Ce(OTf)_4{\cdot}xH_2O$ (5 mg) and 50% (aqueous) H_2O_2 (0.16 ml, 3.0 mmol) in THF (4 ml) was stirred for 1 h at r.t. After completion of the reaction, solvent was evaporated and the substrate was extracted with ethyl acetate (10 ml × 2), dried with anhydrous Na_2SO_4, filtered and evaporated to afford the crude sulfoxide product. Finally the product was purified by column chromatography using ethyl acetate/hexane as eluent to give methyl phenyl sulfoxide as a colorless liquid **1b** in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (s, 3 H, –SO–CH_3), 7.46–7.56 (m, 3 H, ArH), 7.62–7.64 (m, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.8, 123.2, 129.1, 130.8, 145.2; IR (neat): 3012, 2925, 1650, 1450, 1091, 1040, 753 cm^{-1}; EIMS (*m*/*z*): (M^++1) 141; Anal. Calcd for C_7H_8OS: C, 59.97; H, 5.75. Found: C, 59.76; H, 5.90.

*4.1.1. Hexyl phenyl sulfoxide (**2b**)*

IR (neat): 2966, 2868, 1450, 1096, 1045, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 6.8 Hz, –CH_3), 1.24–1.30 (m, 4 H, 2 –CH_2–), 1.33–1.45 (m, 2 H, –CH_2–), 1.55–1.66 (m, 1 H), 1.70–1.80 (m, 1 H), 2.80 (t, *J* = 5.2 Hz, 2 H, –SO–CH_2–), 7.44–7.54 (m, 3 H, ArH), 7.58–7.62 (m, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.1, 22.4, 28.3, 31.3, 57.1, 123.8, 128.9, 130.8, 143.4; EIMS: (M^++1) 211; Anal. Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63. Found: C, 68.64; H, 8.51.

*4.1.2. Ethyl-2-(phenylsulfinyl) acetate (**3b**)*

IR (neat): 2991, 2935, 1742, 1450, 1276, 1096, 1050, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, *J* = 7.2 Hz, –CH_3), 3.66 (d, *J* = 13.6 Hz, 1 H), 3.85 (d, *J* = 13.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, –OCH_2–), 7.51–7.53 (m, 3 H, ArH), 7.67–7.70 (m, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 61.4, 62.0, 124.1, 129.2, 131.7, 142.6, 164.4; EIMS: (M^++1) 213; Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70. Found: C, 56.64; H, 5.68.

*4.1.3. 4-(Phenylsufinyl)butyl acetate (**4b**)*

IR (neat): 2966, 1737, 1455, 1250, 1091, 1040, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.65–1.81 (m, 4 H, 2 –CH_2–), 2.00 (s, 3 H, –$COCH_3$), 2.80 (t, *J* = 6.4 Hz, 2 H, –$SOCH_2$–), 4.00 (t, *J* = 6.0 Hz, –OCH_2–), 7.45–7.50 (m, 3 H, ArH), 7.56–7.58 (m, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 21.11, 27.9, 56.6, 63.6, 124.0, 129.2, 131.1, 143.4, 170.9; EIMS: (M^++1) 241; Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 60.12; H, 6.64.

*4.1.4. 2-(Benzylsulfinyl) ethanol (**5b**)*

IR (neat): 3498, 2930, 1301, 1127, 1081, 1025, 774 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.80 (m, –$SOCH_2^-$), 3.50 (bs, 1 H, –OH), 4.10–4.16 (m, 4 H, 2× –CH_2–), 7.36–7.41 (m, 5 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.8, 56.7, 58.6, 128.8, 129.3, 129.6, 130.4; EIMS: (M^++1) 171; Anal. Calcd for $C_9H_{12}O_2S$: C, 58.67; H, 6.56. Found: C, 58.83; H, 6.72.

*4.1.5. 2-(Pentylsulfinyl) ethanol (**6b**)*

IR (neat): 3426, 2960, 2935, 2863, 1271, 1127, 1066, 1050, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, *J* = 6.8 Hz, 3 H, –CH_3), 1.25–1.46 (m, 4 H, 2 –CH_2–), 1.82–1.90 (m, 2 H, –CH_2–), 2.70 (bs, 1 H, –OH), 3.05–3.10 (m, 2 H, –CH_2–), 3.18–3.21 (m, 2 H, –CH_2–), 4.10–4.13 (m, –CH_2–); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.8, 22.5, 30.8, 54.8, 55.0, 56.6. EIMS: (M^++1) 165; Anal. Calcd for $C_7H_{16}O_2S$: C, 51.18; H, 9.82 Found: C, 51.37; H, 9.78.

*4.1.6. 4-Bromophenylethyl sulfoxide (**7b**)*

IR (neat): 2986, 2879, 1470, 1388, 1086, 1045, 830 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, *J* = 7.6 Hz, 3 H, –CH_3), 2.73–2.80 (m, 1 H), 2.87–2.94 (m, 1 H), 7.47 (d, *J* = 8.4 Hz, 2 H, ArH), 7.64 (d, *J* = 8.4 Hz, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 6.0, 50.2, 125.3, 125.8, 132.3, 142.0; EIMS: (M^++1) 234; Anal. Calcd for C_8H_9BrOS: C, 41.22; H, 3.89. Found: C, 41.55; H, 4.12.

*4.1.7. Dichlorofluoromethyl phenyl sulfoxide (**8b**)*

IR (neat): 3068, 1122, 1076, 866, 805, 748, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.66 (m, 3 H, ArH), 7.82–7.84 (m, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.1 (d, *J* = 339.4 Hz), 127.1, 129.1, 133.7, 137.7; ^{19}F NMR (376 Hz, $CDCl_3$–C_6F_6); δ −98.61 (s, 1 F, –$CFCl_2$–); EIMS: (M^++1) 141.

*4.1.8. 3-(Phenylsulfinyl)propanenitrile (**9b**)*

IR (neat): 2976, 2847, 2250, 1455, 1050, 1025, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48–2.56 (m, 1 H), 2.83–3.00 (m, 2 H), 3.20–3.27 (m, 1 H), 7.53–7.60 (m, 5 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.8, 50.3, 117.3, 123.9, 129.6, 131.7, 141.0; EIMS: (M^++1) 180; Anal. Calcd for C_9H_9NOS: C, 60.31; H, 5.06. Found: C, 60.58; H, 5.24.

*4.1.9. Benzylphenyl sulfoxide (**10b**)*

IR (neat): 3032, 2971, 1455, 1317, 1163, 1096, 1045, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97 (d, *J* = 12.8 Hz, 1 H), 4.06 (d, *J* = 12.8 Hz, 1 H), 6.95 (d, *J* = 6.8 Hz, 2 H, ArH), 7.20–7.27 (m, 3 H, ArH), 7.34–7.45

(m, 5 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.7, 124.4, 128.2, 128.4, 128.8, 129.1, 130.3, 131.1, 142.7; EIMS: (M^++1) 217; Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 72.57; H, 5.22.

*4.1.10. 1-(Allylsulfinyl) benzene (**11b**)*

IR (neat): 3068, 2925, 1644, 1455, 1322, 1148, 1086, 1004, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (d, J = 7.2 Hz, 2 H), 5.14 (d, J = 17.2 Hz, 1 H), 5.31 (d, J = 10.4 Hz, 1 H), 5.72–5.82 (m, 1 H), 7.52–7.56 (m, 2 H, ArH), 7.62–7.65 (m, 1 H, ArH), 7.84–7.87 (m, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.9, 124.6, 124.7, 128.4, 129.0, 133.7, 138.2; EIMS: (M^++1) 167; Anal. Calcd for $C_9H_{10}OS$: C, 65.03; H, 6.06. Found: C, 65.14; H, 6.16.

*4.1.11. Dibenzyl sulfoxide (**12b**)*

IR (neat): 3032, 1465, 1224, 1086, 1040, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (d, J = 10.4 Hz, 4 H), 7.27–7.30 (m, 5 H, ArH), 7.34–7.39 (m, 5 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.4, 128.4, 128.9, 130.1, 130.9; EIMS: (M^++1) 231; Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: C, 73.38; H, 6.24.

*4.1.12. 9-Sulfinyl fluorene (**13b**)*

IR (neat): 2935, 2863, 1650, 1465, 1224, 10876, 1025, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.48 (m, 2 H, ArH), 7.53–7.57 (m, 2 H, ArH), 7.76 (d, J = 7.6 Hz, 2 H, ArH), 7.94 (d, J = 7.6 Hz, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.0, 127.5, 129.6, 132.6, 137.1, 144.9; EIMS: (M^++1) 201; Anal. Calcd for $C_{12}H_8OS$: C, 71.97; H, 4.03. Found: C, 80.13; H, 4.18.

*4.1.13. 1-(Hexylsulfinyl) hexadecane (**14b**)*

IR (neat): 2919, 2848, 1470, 1096, 1025, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80–0.82 (m, 6 H, 2× $-CH_3$), 1.18–1.25 (m, 28 H, 14× $-CH_2-$), 1.35–1.38 (m, 4 H, 2× $-CH_2-$), 1.66–1.70 (m, 4 H, 2× $-CH_2-$), 2.51–2.65 (m, 4 H, 2× $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 14.4, 22.7, 22.8, 22.9, 28.8, 29.1, 29.5, 29.6(2c), 29.7, 29.8(2C), 29.90(3c), 29.92(3C), 31.6, 32.2, 52.6; EIMS: (M^++1) 359; Anal. Calcd for $C_{22}H_{46}OS$: C, 73.67; H, 12.93. Found: C, 73.78; H, 12.80.

*4.1.14. 1-(Hexylsulfinyl) dodecane (**15b**)*

IR (neat): 2960, 2858, 1475, 1015, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86–0.91 (m, 6 H, 2× $-CH_3$), 1.26–1.34 (m, 20 H, 10× $-CH_2-$), 1.40–1.50 (m, 4 H, 2× $-CH_2-$), 1.70–1.80 (m, 4 H, 2× $-CH_2-$), 2.60–2.71 (m, 4 H, 2× $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.3, 22.6, 22.7, 22.8, 22.9, 28.8, 29.1, 29.4, 29.5, 29.6, 29.7, 29.8(2C), 31.6, 32.1, 52.6(2C); EIMS: (M^++1) 303; Anal. Calcd for $C_{18}H_{38}OS$: C, 71.46; H, 12.66. Found: C, 71.35; H, 12.83.

*4.1.15. Dibutylsulfoxide (**16b**)*

IR (neat): 2966, 2879, 1470, 1081, 1035, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, J = 7.2 Hz, 6 H, 2× $-CH_3$), 1.45–1.55 (m, 4 H, 2× $-CH_2-$), 1.71–1.80 (m, 4 H, 2× $-CH_2-$), 2.60–2.72 (m, 4 H, 2× $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 22.1, 24.7, 52.1; EIMS: (M^++1) 163; Anal. Calcd for $C_8H_{18}OS$: C, 59.21; H, 11.18. Found: C, 59.52; H, 11.04.

*4.1.16. 3-(Butylsulfinyl)propanenitrile (**17b**)*

IR (neat): 2971, 2884, 2241, 1650, 1429, 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, J = 7.2 Hz, 3 H, $-CH_3$), 1.44–1.52 (m, 2 H, $-CH_2-$), 1.70–1.77 (m, 2 H, $-CH_2-$), 2.66–3.00 (m, 6 H, 3 $-CH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 13.8, 22.4, 24.7, 46.4, 52.2, 117.6; EIMS: (M^++1) 160; Anal. Calcd for $C_7H_{13}NOS$: C, 52.80; H, 8.23. Found: C, 52.93; H, 8.42.

*4.1.17. 3-(Methylsulfinyl)benzaldehyde (**18b**)*

IR (neat): 2930, 2858, 1711, 1424, 1209, 1096, 1040, 835, 774 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.80 (s, 3 H, $-CH_3$), 7.81 (d, J = 8.2 Hz, 2 H, ArH), 8.00 (d, J = 8.2 Hz, 2 H, ArH), 10.10 (s, 1 H, –CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.9, 124.2, 130.4, 138.1, 152.4, 191.0; EIMS: (M^++1) 169; Anal. Calcd for $C_8H_8O_2S$: C, 57.12; H, 4.79. Found: C, 57.32; H, 4.57.

*4.1.18. 4-Chlorophenyl-4-nitrophenyl sulfoxide (**19b**)*

IR (neat): 3038, 2914, 1521, 1465, 1342, 1086, 1061, 1004, 820, 707 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 2 H, ArH), 7.59 (d, J = 8.4 Hz, 2 H, ArH), 7.79 (d, J = 8.4 Hz, 2 H, ArH), 8.29 (d, J = 8.4 Hz, 2 H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.8, 125.5, 126.4, 130.4, 138.6, 143.1, 149.6, 152.7; EIMS: (M^++1) 283; Anal. Calcd for $C_{12}H_8ClNO_3S$: C, 51.16; H, 2.86; N, 4.97. Found: C, 51.34; H, 2.52; N, 5.12.

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