Tungstate-exchanged Mg-Al-LDH catalyst: an eco-compatible route for the oxidation of sulfides in aqueous medium †

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The catalytic oxidation of sulfides selectively to sulfoxides and/or sulfones is realised for the first time with heterogeneous tungstate-exchanged Mg-Al-LDH catalyst using 30% hydrogen peroxide in aqueous media at a faster rate in quantitative yields at room temperature. The heterogeneous catalyst showed higher activity (TOF) over its homogeneous analogues and other heterogeneous catalysts reported so far. The catalyst is well characterised by various instrumental techniques such as FT-IR spectroscopy, thermal analysis (TGA and DTA), powder XRD and chemical analysis. The catalyst is reused for six cycles with consistent activity and selectivity.

Introduction

The vast chemistry of sulfoxides and sulfones makes them very useful reagents in organic synthesis in general and useful synthetic intermediates for the construction of various chemically and biologically significant molecules in particular.[1] For this reason the oxidation of sulfides to chiral/achiral sulfoxides or sulfones has been the subject of extensive studies and a number of synthetic procedures are now available.[2–18] To date the most important method for preparing sulfoxides or sulfones involves the oxidation of sulfides. Various oxidising reagents used for this purpose include nitric acid,[3] $KMnO_4$,[4] MnO_2,[5] $NaClO_4$,[6] *m*-chloroperbenzoic acid,[7] sodium metaperiodate,[8] bromine,[9] nitrogen tetraoxide,[10,11] oxaziridine,[12] benzeneseleninic peracid,[13] *tert*-butyl hydroperoxide,[14] sulfinyl peroxy compounds,[15] iodosobenzene diacetate[16] and 4-methylmorpholine *N*-oxide with osmium tetraoxide.[17] 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 unfavourable by-products, and high cost. Singlet oxygen or molecular oxygen combined with 2-methylpropanal and Co(II) complexes[18,19] has also been used.

Catalytic homogeneous reactions are preferred over reactions that use stoichiometric quantities, since the stoichiometric reactions are not only corrosive and hazardous, but they also generate copious amounts of heavy metal waste. Aqueous hydrogen peroxide (30%) is an ideal oxidant in view of its high effective-oxygen content (as high as 47%), cleanliness (it produces only water as by-product), safety in storage and operation, and low cost of production and transportation.[20] These obvious advantages have spurred the development of useful procedures for H_2O_2 mediated oxidation of sulfides catalysed by tungsten systems comprising H_2WO_4,[21] $[C_5H_5N(n\text{-}C_{16}H_{33})]_3PO_4[W(O)(O_2)_2]_4$,[22] and $Na_2WO_4 + [n\text{-}C_4H_9)_4N]Cl$[23] in addition to $Na_2MoO_4 + (n\text{-}C_4H_9)_3PO$,[24] $Ti(III)Cl$,[25] CH_3ReO_3.[26] However, there remains much room for improvement, because many of these procedures require chlorohydrocarbon solvents that affect human health and the environment. In order to address this issue recently, Noyori *et al.* reported oxidation of sulfides to sulfoxides and sulfones with 30% H_2O_2 using Na_2WO_4 under solvent and halogen free conditions.[27] A phosphonic acid promoter, and an acidic quaternary ammonium salt, $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, are used along with the catalyst which

makes the process cumbersome. Moreover the catalyst could not be recovered for further cycles.

An ideal system for such reactions is the use of solid catalysts under heterogeneous conditions, which allows easy separation of the catalysts from the reaction mixture and adaptability in large-scale production to conform to the class of greener technologies. In recent years selective oxidation of sulfides to sulfoxides or sulfones has been carried out with a large number of supported reagents or catalysts.[28] For instance, titanium silicates (TS-1 and TS-2)[28g] promote sulfide oxidation, but the use of bulky sulfides is precluded by their limited access to the Ti active sites. In order to overcome this limitation, mesoporous materials have been used. Ti-MCM-41 allows the oxidation of bulky sulfides[29] but with the loss of selectivity. Recently Fraile *et al.* introduced $Ti(OiPr)_4$ supported on silica as an efficient and selective catalyst for the oxidation of sulfides to sulfoxides,[30] but the drawback is the gradual leaching of titanium during the reaction.

With an ever-increasing level of global competition and environmental consciousness, there is much incentive to find new and strategically important processes using a highly robust and recyclable catalyst that provides higher atom utilisation, preferably close to theoretical values, to eventually minimise pollution levels using greener ingredients. The challenge is to perform a truly heterogeneous catalytic reaction for the oxidation of sulfides in the laboratory, bulk and fine chemical industries. Layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTLCs)[31] have recently received much attention in view of their potential usefulness as adsorbents, anion exchangers and most importantly as catalysts.[32] The hydrophilicity of the LDH material makes the hosted oxidation catalyst water compatible to conduct the reactions using water as a solvent. Recently we reported the catalytic N-oxidation of tertiary amines by tungstate-exchanged Mg-Al-LDH catalyst (LDH-WO_4) in quantitative yields at faster rate in aqueous media.[33] We report in this paper an efficient and heterogeneous tungstate-exchanged Mg-Al-LDH catalyst for the oxidation of sulfides using H_2O_2 as an oxidant and water as a solvent with good to excellent yields for the first time (Scheme 1).

Results and discussion

The structure of layered double hydroxides (LDH) consists of brucite [$Mg(OH)_2$] type octahedral layers in which some of the M(II) cations are isomorphously substituted by M(III) cations.

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Table 1 The oxidation of thioanisole using various transition metal oxide exchanged LDH catalysts and their homogeneous analogues[a]

Entry	Catalyst	Time/h	Conversion (%)	1a : 1b	TOF/h$^{-1 b}$
1	LDH-WO$_4^{2-}$ (cat **1**)	0.5	94	88 : 12	42.72
2	LDH-MoO$_4^{2-}$ (cat **2**)	3.0	80	94 : 6	4.4
3	LDH-VO$_3^-$ (cat **3**)	3.5	42	100 : 0	1.53
4	LDH-{PO$_4$WO(O$_2$)]$_4$} (cat **4**)	4.0	90	40 : 60	15
5	Na$_2$WO$_4$	2.5	95	70 : 30	9
6	NaVO$_3$	4.0	35	80 : 20	4.2
7	Na$_2$MoO$_4$	3.5	89	94 : 6	1.12
8	None	6.0	No reaction	—	—

[a] All reactions were carried out with 2 mmol of substrate, 200 mg of catalyst in 10 cm^3 of water, 0.66 cm^3 (6 mmol) of aqueous hydrogen peroxide (30% w/w). [b] TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.
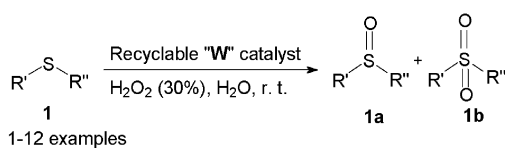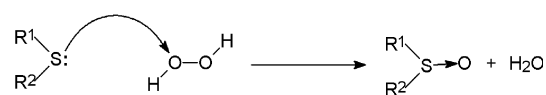

Scheme 1

The excess positive charge of the octahedral layers resulting from this substitution is compensated by interstitial layers built of anions such as carbonate, nitrate, chlorides, cyanide and crystal water. The redox properties of LDH can be tunable or imparted according to the requirements. This can be done in different ways, one being the introduction of redox properties by incorporating a redox divalent or trivalent transition metal ion or both. The other option is the change in the ratios of redox metal ions chosen for the preparation of a specific catalyst. Yet another manner by which the redox properties of the LDH can be tuned or introduced is by incorporating transition metal oxides as anions to neutralise the positive charge developed as a result of the isomorphous substitution of Mg in the brucite main frame as discussed above. These LDHs are thus represented by the general formula $[M(II)_{(1-x)}M(III)_x(OH)_2]^{x+}[(A^{y-})_{x/y}\cdot nH_2O]^{x-}$ where $M(II)$ is a divalent cation such as Mg, Cu, Ni, Co, Mn, Fe, Zn; $M(III)$ is a trivalent cation such as Al, Fe, Cr, V, Ru, Rh, Ga, In; A^{n-} is the interlayer anion such as OH$^-$, Cl$^-$, CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$ and the value of x is in the range of 0.1 to 0.33. The small hexagonal LDH crystals with Mg$_{1-x}$Al$_x$(OH)$_2$(Cl)$_x\cdot z$H$_2$O composition were synthesized following existing procedures (here, $x = 0.25$).[34] The anionic species tungstate, molybdate, vanadate and {PO$_4$WO(O$_2$)]$_4$}$^{-2}$ were exchanged on to LDH-Cl to give a series of LDH oxidant catalysts, LDH-WO$_4$ (cat **1**),[32e] LDH-MoO$_4$ (cat **2**) LDH-VO$_3$ (cat **3**) and LDH-{PO$_4$WO(O$_2$)]$_4$} (cat **4**) respectively.

All these catalysts are well characterised by XRD, TGA–DTA and chemical analysis. The X-ray powder diffraction patterns of the LDH and LDH-WO$_4$ (cat **1**), LDH-MoO$_4$ (cat **2**), LDH-VO$_3$ (cat **3**), LDH-{PO$_4$WO(O$_2$)]$_4$} (cat **4**) hardly differ in the range of $2\theta = 3$–65°. These data clearly indicate that the above anions are not intercalated but present at the edge-on positions of the LDH in the solid catalyst. Chemical analysis of the catalysts shows that the tungstate content (%) in cat **1** = 11 and cat **4** = 21, molybdate content in cat **2** = 9.9, and vanadate content in cat **3** = 7.8. The thermogravimetric profiles and the relative derivative curves (TGA and DTA) for the tungstate, molybdate and vanadate exchanged LDH catalysts cat **1**, cat **2**, cat **3** and cat **4** show two stages of weight loss associated with two endotherms, which represents the characteristic pattern of the LDH structure. These results indicate that there was no structural disorder after the ion exchange.

The exchanged LDH catalysts (cat **1**–**4**) and their homogeneous analogues were evaluated for the oxidation of thioanisole in order to identify the best catalytic system using H$_2$O$_2$ in aqueous medium (Table 1). The order of the activity of

layered double hydroxides supported catalysts is cat **1** > cat **2** > cat **4** > cat **3**. The heterogeneous catalysts displayed superior activity over their homogeneous counterparts. LDH-WO$_4$ (cat **1**) exhibited the highest (molar) turnover frequency of 21.7 h^{-1} over the other exchanged LDH catalysts. Besides this, the exchanged LDH catalysts showed 2–5 fold activity over the analogous homogeneous catalytic systems. This is a very significant result over Noyori's recently reported procedure,[27] an analogous reaction conducted with Na$_2$WO$_4$ wherein the additives and moderate temperatures are required to accomplish the reaction in excellent yields. Thus LDH-WO$_4$ (cat **1**) is proved to be the best catalyst among the various exchanged LDH catalysts and their homogeneous analogues, for the oxidation of sulfides. No reaction occurred without catalyst, in the oxidation of thioanisole (Table 1, entry 8). The enrichment of sulfides on the surface of water compatible ionic LDH and the ready formation of peroxide with the tungstate of LDH are likely to contribute to the enhancement of reactivity in the oxidation of sulfides using LDH-WO$_4$ catalyst.
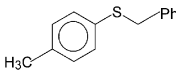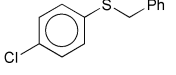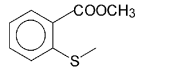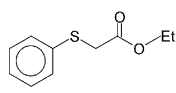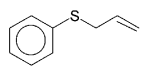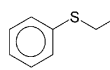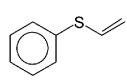
In an effort to understand the scope of the reaction, a series of sulfides having different kinds of R groups attached to the sulfur atom were subjected to the oxidation using the LDH-WO$_4$–H$_2$O$_2$ system and the results are presented in Table 2. Aromatic sulfides, which are selectively oxidised to sulfoxides at lower conversions and lower time intervals, are converted to sulfones on prolonged reaction times (Table 2, entries 1–8). On the other hand aliphatic sulfides are oxidised at faster rate than the aromatic sulfides (Table 2, entries 10–12). Further, the oxidations of aliphatic sulfides do not proceed to form sulfones selectively even on prolonged reaction times. It is known that organic sulfides are oxidised by hydrogen peroxide in a heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen according to Scheme 2.[28f] The rate of the
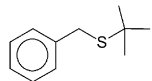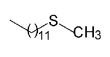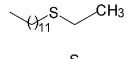

Scheme 2

oxidation of thioethers increases with the increased nucleophilicity on the sulfur atom. The dialkyl sulfides are thus indeed more easily oxidised than the diaryl sulfides using the LDH-WO$_4$–H$_2$O$_2$ catalytic system. Similarly, due to the decreased nucleophilicity prompted by conjugation, the allylic and vinylic sulfides (Table 2, entries 6, 8) are less reactive than the dialkyl sulfide. It is significant to note that the allylic and vinylic sulfides form corresponding sulfoxides without the breaking of carbon–carbon bonds.

The studies on the conversion/selectivity as a function of time in the oxidation of sulfides was carried out with three of the substrates (Table 2, entries 2, 6 and 7). The studies show higher selectivities towards sulfoxides at lower conversions. With increasing time, the conversion increases while the

Table 2 The oxidation of sulfides by tungstate-exchanged Mg-Al-LDH catalyst[a]

Entry	Sulfide 1–12	Time/h	Conversion (%)	Sulfoxide 1a–12a	Sulfone–10b
1	(thioanisole)	0.5	94	88	12
			90[b]	85	15
2	(4-methylbenzyl phenyl sulfide)	3.0	87	88	12
		7.0	95	60	40
		12.0	99	1	99
3	(4-chlorobenzyl phenyl sulfide)	3.0	99	90	10
4	(methyl 2-(methylthio)benzoate)	3.0	91	95	5
5	(ethyl (phenylthio)acetate)	3.0	91	95	5
6	(allyl phenyl sulfide)	3.0	81	70	30
		7.0	94	45	55
		12.0	98	1	99
7	(ethyl phenyl sulfide)	3.0	78	83	17
		7.0	96	43	57
		12.0	99	1	99
8	(phenyl vinyl sulfide)	3.0	99	71	29
9	(benzyl tert-butyl sulfide)	2.0	99	90	10
10	(undecyl methyl sulfide)	1.5	99	80	20
11	(undecyl ethyl sulfide)	1.5	99	100	—
12	(cyclohexyl methyl sulfide)	1.5	98	100	—

[a] Reaction conditions are as exemplified in Table 1, in footnote a. [b] Conversion after 6th cycle.
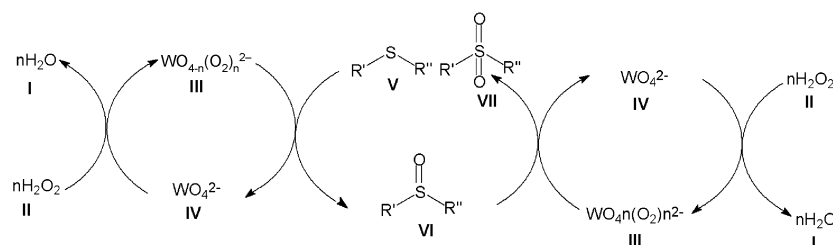
Scheme 3

selectivity is reduced. The maximum selectivity of 100% is achieved at 54–62% of conversion. It is always better to terminate the reaction at these conversions in order to obtain sulfoxides of high purity.

The solvent effect was also studied in the oxidation of thioanisole using LDH-WO$_4$ catalyst; the activity is in the following order: H$_2$O ≅ CH$_3$OH > CHCl$_3$ > CH$_3$CN > CH$_2$Cl$_2$. Thus water gave the best results among the solvents examined in the oxidation of sulfides. Furthermore the reusability was checked for several cycles with the best catalyst, cat **1**, which showed consistent activity and selectivity for six cycles as detailed in Table 2, entry 1. During the oxidation with WO$_4^{2-}$ 0.3% of the total amount of tungsten was found in solution and the use of recycled catalysts resulted in unaltered activity, supporting the oxidative stability of the catalyst.

The plausible catalytic cycle in the oxidation of sulfides to sulfoxides or sulfones as described in Scheme 3 involves the easy formation of peroxotungstate, **IV**, on interaction of LDH-WO$_4$

III with hydrogen peroxide **II**.[32e] A shift of λ_{max} from 250 nm (LDH **III**) to 325 nm (**IV**) in UV–diffusion reflectance spectra confirms the formation of peroxotungstate species. Our system and hydrogen peroxide directed oxidation of sulfides show similar trends in reactivity *i.e.* aliphatic sulfides are oxidised at faster rate than aromatic sulfides due to the higher nucleophilicity of aliphatic sulfides. In the present reaction the facilitation of the transfer of electrophilic oxygen from the peroxotungstate species, **IV**, to sulfide **V** forming sulfoxide **VI**, is commensurate with the nucleophilicity of the sulfides, *i.e.*, the rate of the reaction is increased as the nucleophilicity increases. Further, the electrophilicity of the peroxotungstate is much higher than that of H$_2$O$_2$. Therefore the electrophilic attack of oxygen in the bridged tungsten oxide is faster, which is in agreement with earlier results.[35] In case of sulfone formation, the sulfoxide **VI** further reacts with the another mole of active peroxotungstate, **IV** to form sulfone **VII** and the eventual regeneration of the catalyst **III**.

Conclusions

In conclusion, the present study represents the first example wherein the heterogenised tungstate-exchanged Mg-Al-LDH is used in catalytic amounts for the oxidation of sulfides to sulfoxides and/or sulfones. With the broader scope of utility as applied for bulky sulfoxides and consistent activity over a number of cycles, the present catalytic system is superior to the other heterogeneous catalysts reported so far. The high throughput of the product obtained using the LDH-WO₄ catalyst lowers the inventories of the process to offer a potential competitive economically viable process. The use of water as solvent and H_2O_2 as an oxidant, which are greener ingredients, conforms to the stringent environmental specifications.

Experimental

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Gemini Varian at 200 or 400 MHz, as solutions in CDCl₃ at 25 °C; δ were in ppm downfield from tetramethylsilane (TMS). Mass spectra were obtained at an ionization potential of 70 eV, scanned on a VG 70–70H (micro mass); only selected ions are reported here. Infrared spectra were recorded on a Bio-RAD FT-IR spectrometer either as neat liquids or KBr pellets. Thin layer chromatography was performed on silica gel 60F₂₅₄ plates procured from E. Merck. ACME silica gel (60–120 mesh) was used for column chromatography. Starting materials, metal salts were purchased from Aldrich, Fluka, and Lancaster or prepared by known methods. Solvents purchased from commercial sources were purified prior to use. Thermogravimetric (TG) and differential thermogravimetric (DT) analysis of thermal decomposition of catalyst was studied by means of a TG-DTA Mettler Toledo Star system using open aluminium crucibles with a sample weight of about 8–10 mg and nitrogen as purge gas at a linear heating rate of 10 K min^{-1} for all measurements. X-Ray diffraction patterns were determined on a powder X-ray diffractometer Siemens, D-5000 (diffraction geometry; θ–2θ, in the range of 5–65°) instrument, using sealed Cu tube (2.2 kW). CHN analysis was performed on a Vario EL analyser.

Preparation of catalysts

Mg-Al-LDH chloride.[34] Mg-Al-Cl LDH (3 : 1) was prepared as follows: a mixture of solutions of AlCl₃·9H₂O (12.07 g, 0.25 mol l^{-1}) and MgCl₂·6H₂O (30.49 g, 0.75 mol l^{-1}) in deionised and decarbonated water (200 cm³) and an aqueous solution of sodium hydroxide (16 g, 2 mol l^{-1}) in deionised and decarbonated water (200 cm³) were added simultaneously dropwise from the respective burettes into the round bottomed flask. The pH of the reaction mixture was maintained constant (10.00–10.2) by the continuous addition of NaOH solution. The suspension thus obtained was stirred for two hours under nitrogen atmosphere. The solid product was isolated by filtration, washed thoroughly with deionised and decarbonated water, and dried at 70 °C for 15 h.

Mg-Al-LDH tungstate (cat 1).[32e] To a solution of sodium tungstate (0.616 g, 1.87 mM) in water (100 cm³), Mg-Al-Cl LDH (1 g) was added and stirred at 293 K for 24 h. The solid catalyst was filtered, washed with deionised and decarbonated water and lyophilized to dryness.

Mg-Al-LDH molybdate (cat 2). To a solution of sodium molybdate (0.452 g, 1.87 mM) in water (100 cm³), Mg-Al-Cl LDH (1 g) was added and stirred at 293 K for 24 h. The solid catalyst was filtered, washed with deionised and decarbonated water and lyophilized to dryness.

Mg-Al-LDH vanadate (cat 3). To a solution of sodium vanadate (0.228 g, 1.87 mM) in water (100 cm³), Mg-Al-Cl

LDH (1 g) was added and stirred at 293 K for 24 h. The solid catalyst was filtered, washed with deionised and decarbonated water and lyophilized to dryness.

Mg-Al-LDH-{PO₄WO(O₂)]₄} (cat 4). The preparation of {PO₄[WO(O₂)₂]₄} ((n-Bu)₄N)₃ was carried out according to the literature procedure.[36] To a solution of isolated {PO₄[WO(O₂)₂]₄} ((n-Bu)₄N)₃ (0.46 mmol) in acetone (3 cm³) was added an aqueous solution of 30% (w/w) H₂O₂ (1 cm³) and Mg-Al-Cl LDH (1 g) and the mixture was stirred for 16 h at room temperature. The obtained material (cat **4**) was treated consecutively with water–acetone (1 : 1) and acetone.

Typical procedure for the oxidation of thioanisole

To the stirred solution of thioanisole (280 mg, 2 mmol) and catalyst (200 mg, 0.088 mmol of WO_4^{2-} content) in water (10 cm³), was added an aqueous solution of 30% (w/w) hydrogen peroxide (0.66 cm³, 6 mmol) in 2 to 3 portions at room temperature. After completion of the reaction (followed by TLC), the catalyst was filtered off and washed with ethyl acetate (2 × 10 cm³). To the filtrate a small amount of MnO₂ was added to decompose the unreacted H₂O₂. The treated reaction mixture was filtered to remove solid MnO₂, and the product is extracted with ethyl acetate, dried over anhydrous Na₂SO₄ and evaporated *in vacuo* to afford the sulfoxide or sulfone. Analytically pure compound was obtained after column chromatography (silica gel, hexane–ethyl acetate)

The products were characterised by their ^{1}H NMR, mass, IR spectroscopy and elemental analysis and the data are presented below.

Methylsulfinylbenzene 1a.[37] Pale yellow liquid (Found: C, 59.84; H, 5.67; S, 22.63. C₇H₈SO requires C, 60.0; H, 5.71; S, 22.85%); ν_{max}(neat)/cm^{-1} 1047; δ_H (200 MHz; CDCl₃; Me₄Si) 2.78 (3H, s, Me), 7.44–7.66 (m, 5H, Ph); *m/z* (EI), 140 (M⁺, 87%), 125 (100), 109 (71), 77 (69), 65 (19) 51 (70), 39 (15).

Methylsulfonylbenzene 1b. White solid, mp 85–86 °C (lit.,[37] 85–86 °C) (Found: C, 53.62; H, 5.01; S, 20.32. C₇H₈SO₂ requires C, 53.84; H, 5.12; S, 20.51%); ν_{max}(KBr)/cm^{-1} 1320, 1164; δ_H (200 MHz; CDCl₃; Me₄Si) 3.0 (3H, s, Me), 7.44–7.64 (m, 3H, Ph), 7.84–7.95 (2H, d, Ph–H, J = 8.1 Hz); *m/z* (EI), 156 (M⁺, 22%), 142 (27), 77 (100), 65 (8), 51 (37).

1-Benzylsulfinyl-4-methylbenzene 2a. White solid, mp 122–124 °C (Found: C, 73.25; H, 6.12; S, 13.81. C₁₄H₁₄SO requires C, 73.04; H, 6.08; S, 13.91%); ν_{max}/cm^{-1} 1038; δ_H (200 MHz; CDCl₃; Me₄Si) 2.4 (3H, s, Me), 3.9 (1H, d, CH₂, J = 12.7 Hz), 4.05 (1H, d, CH₂, J = 12.7 Hz), 6.9 (m, 2H, Ph–H) 7.18 (m, 7H, Ph–H); *m/z* (EI), 230 (M⁺, 5%), 91 (100), 65 (81), 51 (12).

1-Benzylsulfonyl-4-methylbenzene 2b. White solid, mp 142–144 °C (Found: C, 68.32; H, 5.68; S, 13. 28. C₁₄H₁₄SO₂ requires C, 68.29; H, 5.69; S, 13.00%); ν_{max}(KBr)/cm^{-1} 1309, 1151; δ_H (200 MHz; CDCl₃; Me₄Si) 2.42 (3H, s, Me), 4.22 (2H, s, CH₂), 7.06 (m, 2H, Ph–H), 7.22 (m, 3H, Ph–H), 7.4 (m, 2H, Ph–H), 7.62 (m, 2H, Ph–H); *m/z* (EI), 246 (M⁺, 6%) 230 (4), 91 (100), 65 (82) 51 (15), 39 (45).

1-Benzylsulfinyl-4-chlorobenzene 3a. White solid, mp 120–122 °C (Found: C, 62.24; H, 4.47; S, 12.72; Cl, 14.13. C₁₃H₁₁SOCl requires C, 62.40; H, 4.40; S, 12.80; Cl, 14.20%); ν_{max} (KBr)/cm^{-1} 1040; δ_H (200 MHz; CDCl₃; Me₄Si) 3.98 (1H, d, CH₂, J = 12.7 Hz), 4.04 (1H, d, CH₂ J = 12.7 Hz), 6.95 (2H, d, Ph–H, J = 6.8 Hz), 7.3 (5H, m, Ph–H), 7.38 (2H, d, Ph–H, J = 6.8 Hz); *m/z* (EI), 252 (M⁺, (³⁷Cl) 2%), 250 (M⁺, (³⁵Cl) 6), 234 (66), 143 (10), 108 (11), 91 (100), 65 (62), 51 (7).

1-Benzylsulfonyl-4-chlorobenzene 3b. White solid, mp 142–145 °C (Found: C, 58.88; H, 4.17; S, 11.97; Cl, 13.38. $C_{13}H_{11}SO_2Cl$ requires C, 58.64; H, 4.13; S, 12.03; Cl, 13.34%); v_{max}(KBr) /cm^{-1} 1310, 1150; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 4.24 (2H, s, CH$_2$), 7.01 (2H, d, Ph–H, J = 6.8 Hz), 7.32 (3H, m, Ph–H), 7.42 (2H, d, Ph–H, J = 6.8 Hz), 7.58 (2H, d, Ph–H, J = 6.8 Hz); m/z (EI), 268 (M$^+$, (^{37}Cl) 4%), 266 (M$^+$, (^{35}Cl) 12), 250 (8), 91 (100), 65 (42), 51 (11).

Methyl 2-methylsulfinylbenzoate 4a. Pale yellow liquid (Found: C, 54.36; H, 5.36; S, 16.25. $C_9H_{10}SO_3$ requires C, 54.54; H, 5.05; S, 16.16%); v_{max}(KBr) /cm^{-1} 1067; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 2.85 (3H, s, SOMe), 3.95 (s, 3H, OMe), 7.58 (1H, t, Ph–H, J = 7.2 Hz), 7.85 (1H, t, Ph–H, J = 7.2 Hz), 8.05 (1H, d, Ph–H, J = 6.8 Hz), 8.32 (1H, d, Ph–H, J = 7.2 Hz); m/z (EI), 198 (M$^+$, 30%), 183 (100), 167 (10), 152 (45), 77 (12).

Methyl 2-methylsulfonylbenzoate 4b. Pale yellow viscous liquid (Found C, 50.62; H, 4.68; S, 14.98. $C_9H_{10}SO_4$ requires C, 50.46; H, 4.67; S, 14.96%); v_{max}(neat)/cm^{-1} 1311, 1153; δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 3.3 (3H, s, SO$_2$Me), 3.98 (3H, s, OMe), 7.62 (3H, m, Ph–H), 8.1 (1H, d, Ph–H, J = 6.4 Hz); m/z (EI), 214 (M$^+$, 6%), 199 (10), 183 (100), 135 (8), 77 (36).

Ethyl 2-phenylsulfinylacetate 5a. Pale yellow liquid (Found: C, 56.58; H, 5.54; S, 15.22. $C_{10}H_{12}SO_3$ requires C, 56.60; H, 5.66; S, 15.09%); v_{max}(neat)/cm^{-1} 1043; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 1.3 (3H, t, Me, J = 7.5 Hz), 3.62 (1H, d, SCH$_2$, J = 12.5 Hz), 3.85 (1H, d, SCH$_2$, J = 12.5 Hz), 4.15 (2H, q, OCH$_2$, J = 7.5 Hz), 7.55 (m, 3H, Ph–H), 7.7 (m, 2H, Ph–H); m/z (EI), 212 (M$^+$, 12%), 196 (7), 140 (8), 125 (100), 110 (25), 77 (86), 65 (14), 51 (47).

Ethyl 2-phenylsulfonylacetate 5b. Pale yellow liquid (Found C, 52.48; H, 5.48; S, 14.23. $C_{10}H_{12}SO_4$ requires C, 52.63; H, 5.26; S, 14.03%); v_{max}(neat)/cm^{-1} 1318, 1145; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 1.25 (3H, t, Me, J = 6.4 Hz), 4.08 (2H, s, SCH$_2$), 4.18 (q, 2H, OCH$_2$, J = 6.4 Hz), 7.6 (2H, t, Ph–H, J = 7.2 Hz), 7.7 (1H, t, Ph–H, J = 7.2 Hz), 7.95 (2H, d, Ph–H, J = 7.2 Hz); m/z (EI), 228 (M$^+$, 2%), 150 (16), 141 (38), 125 (15), 77 (100), 51 (35).

1-Allylsulfinylbenzene 6a.[28h] Pale yellow liquid (Found: C, 65.28; H, 6.12; S, 19.32. $C_9H_{10}SO$ requires C, 65.06; H, 6.02; S, 19.27%); v_{max}(neat)/cm^{-1} 1044; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 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, Ph–H); m/z (EI), 166 (M$^+$, 12%), 141 (10), 125 (56), 117 (30), 109 (8), 97 (25), 65 (10), 51 (53), 41 (100).

1-Allylsulfonylbenzene 6b. Pale yellow liquid (Found: C, 59.46; H, 5.68; S, 17.62. $C_9H_{10}SO_2$ requires C, 59.34; H, 5.49; S, 17.58%); v_{max}(neat)/cm^{-1} 1319, 1147; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 3.8 (d, 2H, CH$_2$, J = 6.6 Hz), 5.18 (1H, d, CH, J = 16.6 Hz), 5.38 (1H, d, CH, J = 11 Hz), 5.8 (1H, m, CH), 7.43–65 (m, 5H, Ph–H); m/z (EI), 182 (M$^+$, 8%), 166 (4), 141 (30), 125 (100), 117 (28), 97 (45), 65 (10), 51 (48), 41 (80).

1-Ethylsulfinylbenzene 7a. Pale yellow liquid (Found: C, 62.49; H, 6.52; S, 21.03. $C_8H_{10}SO$ requires C, 62.33; H, 6.49; S, 20.77%); v_{max}(neat)/cm^{-1} 1062; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 1.2 (3H, t, Me, J = 6.6 Hz), 2.7–2.75 (1H, q, CH$_2$, J = 6.6 Hz), 2.9 (1H, q, CH$_2$, J = 6.6 Hz), 7.1–7.45 (m, 3H, Ph–H), 7.45–7.8 (m, 2H, Ph–H); m/z (EI), 154 (M$^+$, 34%), 138 (14), 126 (62), 109 (86), 77 (100), 51 (94).

1-Ethylsulfonylbenzene 7b. White solid, mp >260 °C (Found: C, 56.43; H, 5.97; S, 18.93. $C_8H_{10}SO_2$ requires C, 56.47; H, 5.88; S, 18.82%); v_{max}(KBr)/cm^{-1} 1320, 1146; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 1.3 (t, 3H, Me, J = 7.0 Hz), 3.1 (2H, q, CH$_2$ J = 7.0 Hz),

7.5 (3H, m, Ph–H), 7.9 (2H, m, Ph–H); m/z (EI), 170(M$^+$, 30%), 154 (35), 126 (50), 109 (65), 77 (100), 51 (60).

1-Vinylsulfinylbenzene 8a.[38] Pale yellow liquid (Found: C, 62.28; H, 5.22; S, 21.13. C_8H_8SO requires C, 63.15; H, 5.26; S, 21.05%); v_{max}(neat) /cm^{-1} 1053; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 5.89 (1H, d, CH, J = 10.2 Hz), 6.2 (1H, d, CH, J = 15.3 Hz), 6.5–6.8 (1H, m, CH), 7.5–7.8 (m, 5H, Ph–H); m/z (EI), 152 (M$^+$, 3%), 135 (26), 125 (70), 109 (30), 91 (37), 77 (100), 51 (60), 40 (28).

(tert-Butylsulfinylmethyl)benzene 9a. Pale yellow solid, mp 72–73 °C (lit.,[39] 72–73 °C) (Found: C, 66.49; H, 8.20; S, 16.49. $C_{11}H_{16}SO$ requires C, 67.34; H, 8.16; S, 16.32%); v_{max}(KBr)/ cm^{-1} 1032; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 1.3 (9H, s, t-Butyl), 3.7 (1H, d, CH$_2$, J = 12.7 Hz), 3.85 (1H, d, CH$_2$, J = 12.7 Hz), 7.35 (5H, m, Ph–H); m/z (EI), 196 (M$^+$, 8%), 140 (39), 91 (100), 65 (8).

(tert-Butylsulfonylmethyl)benzene 9b. Pale yellow solid, mp 117–120 °C (Found: C, 62.42; H, 7.56; S, 15.29. $C_{11}H_{16}SO_2$ requires C, 62.26; H, 7.54; S, 15.09%); v_{max}(neat)/cm^{-1} 1284, 1153; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 1.4 (s, 9H, t-Butyl), 4.15 (2H, s, CH$_2$), 7.4 (m, 5H, Ph–H); m/z (EI), 212 (M$^+$, 3%), 141 (2.5), 91 (32), 57 (100).

1-Methylsulfinyldodecane 10a. White solid, mp 63–65 °C (Found: C, 66.49; H, 12.26; S, 13.68. $C_{13}H_{28}SO$ requires C, 67.24; H, 12.06; S, 13.79%); v_{max}(KBr)/cm^{-1} 1082; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 0.9 (3H, t, Me, J = 6.6 Hz), 1.2–1.6 (18H, m, CH$_2$), 1.7–1.95 (2H, m, CH$_2$), 2.56 (3H, s, SMe), 2.6–2.8 (m, 2H, CH$_2$); m/z (EI), 232 (M$^+$, 2), 216 (20), 201(11), 57 (75), 43 (100) 41 (89).

1-Methylsulfonyldodecane 10b. White solid, mp 80–83 °C (Found: C, 62.79; H, 11.42; S, 13.02. $C_{13}H_{28}SO_2$ requires C, 62.90; H, 11.29; S, 12.90%); v_{max}(KBr) /cm^{-1} 1281, 1118; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 0.98 (3H, t, CH$_3$, J = 7.0 Hz), 1.28 (18H, m, CH$_2$), 1.82 (2H, m, CH$_2$), 2.82 (3H, s, Me), 2.86 (2H, t, CH$_2$, J = 7.0 Hz); m/z (EI), 248 (M$^+$, 8%), 108 (46), 81(100), 69(25), 57(35).

1-Ethylsulfinyldodecane 11a. White solid, mp 68–70 °C (Found: C, 68.44; H, 12.05; S, 13.26. $C_{14}H_{30}SO$ requires C, 68.29; H, 12.19; S, 13.00%); v_{max}(KBr)/cm^{-1} 1046; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 0.9 (3H, t, CH$_3$, J = 6.3 Hz), 1.2–1.5 (m, alkyl, 21H), 1.7–1.9 (2H, m, CH$_2$), 2.55–2.75 (2H, m, CH$_2$), 2.95–3.0 (2H, m, CH$_2$); m/z (EI), 246 (M$^+$, 2%), 229 (100), 95 (25), 71 (50).

Methylsulfinylcyclohexane 12a. Pale yellow liquid (Found: C, 57.66; H, 9.69; S, 21.85. $C_7H_{14}SO$ requires C, 57.53; H, 9.58; S, 21.91%); v_{max}(neat) /cm^{-1} 1036; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 1.2–1.5 (6H, m, CH$_2$), 1.7–2.2 (4H, m, CH), 2.5 (3H, s, CH), 2.8 (1H, m, CH); m/z (EI), 146 (M$^+$, 4%), 83 (95), 55 (100), 41(39).

Acknowledgements

References

1 (*a*) S. Patai and Z. Rappoport, *Synthesis of sulfones, sulfoxides, and cyclic sulfides*, J. Wiley, Chichester, 1994; (*b*) M. Mikolajczyk, *Tetrahedron*, 1986, **42**, 5459.
2 (*a*) J. M. Brunel and H. B. Kagan, *Synlett*, 1996, 404; (*b*) S. H. Di Furia, G. Modena and G. Seraglia, *Synthesis*, 1984, 325; (*c*) C. Bolm and F. Bienwald, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2640.
3 (*a*) C. Marcker, *Ann.*, 1865, **136**, 75; (*b*) F. G. Bordwell and P. Boutan, *J. Am. Chem. Soc.*, 1957, **79**, 717.

4 G. W. Gokel, H. M. Gerdes and D. M. Dishong, *J. Org. Chem.*, 1980, **45**, 3634.

5 D. Edwards and J. B. Stenlake, *J. Chem. Soc.*, 1954, 3272.

6 J. M. Khurana, A. K. Panda, A. Ray and A. Gogia, *Org. Prep. Proced. Int.*, 1996, **28**, 234.

7 T. Durst, *J. Am. Chem. Soc.*, 1969, **91**, 1034.

8 (*a*) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, 1962, **27**, 282; (*b*) C. R. Johnson and J. E. Keiser, *Org. Synth.*, 1973, **Coll. Vol. V**, 791.

9 J. Drabowicz, W. Midura and M. Kolajczyk, *Synthesis*, 1979, 39.

10 Horner and Hubenett, *Annalen*, 1953, **579**, 193.

11 C. C. Addison and J. Sheldon, *J. Chem. Soc.*, 1956, 2705.

12 F. A. Davis, R. Jenkins Jr. and S. G. Yocklovich, *Tetrahedron Lett.*, 1978, 5171.

13 (*a*) H. J. Reich, F. Chow and S. L. Peake, *Synthesis*, 1978, 299; (*b*) K. R. Roh, K. S. Kim and Y. H. Kim, *Tetrahedron Lett.*, 1991, **32**, 793.

14 K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, 1979, **12**, 63.

15 Y. H. Kim and D. C. Yoon, *Tetrahedron Lett.*, 1988, **29**, 6453–6456.

16 R. Takata, Tajima and W. Ando, *Phosphorus, Sulfur Silicon*, 1983, **16**, 67.

17 S. W. Kaldor and M. Hammond, *Tetrahedron Lett.*, 1991, **32**, 5043.

18 V. Khanna, G. C. Maikap and J. Iqbal, *Tetrahedron Lett.*, 1996, **37**, 3367.

19 M. M. Dell'Anna, P. Mastrorilli and C. F. Nobile, *J. Mol. Catal.*, 1996, **108**, 57.

20 (*a*) K. Sato, M. Aoki and R. Noyori, *Science*, 1998, **281**, 1646; (*b*) G. T. Brink, I. W. C. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636.

21 H. S. Schultz, H. B. Freyermuth and S. R. Buc, *J. Org. Chem.*, 1963, **28**, 1140.

22 Y. Ishi, H. Tanaka and Y. Nisiyama, *Chem. Lett.*, 1994, 1.

23 Z. Stec, J. Zawadiac, A. C. Skibinski, H. I. S. Nogueira and B. C. Parkin, *J. Mol. Catal.*, 1997, **117**, 185.

24 O. Bortolini, F. Di Furia, G. Modena and R. Seraglia, *J. Org. Chem.*, 1985, **50**, 2688.

25 Y. Watanabe, T. Numata and S. Oae, *Synthesis*, 1981, 204.

26 S. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2955.

27 K. Sato, M. Hyodo, M. Aoki, Zheng X-Qi and R. Noyori, *Tetrahedron*, 2001, **57**, 2469.

28 (*a*) G. W. Breton, J. D. Fields and P. J. Kropp, *Tetrahedron Lett.*, 1995, **36**, 3825; (*b*) P. Kannan, R. Sevel, S. Rajagopal and K. Pitchumani, *Tetrahedron*, 1997, **53**, 7635; (*c*) R. S. Varna, R. K. Saini and H. M. Meshram, *Tetrahedron Lett.*, 1997, **38**, 6525; (*d*) M. H. Ali and W. C. Stevens, *Synthesis*, 1997, 764; (*e*) M. Hirano, S. Yakbne, S. Itoh, J. H. Clart and T. Morimotoa, *Synthesis*, 1997, 1161; (*f*) V. Hulea, P. Moreau and F. Di Renzo, *J. Mol. Catal. A*, 1996, **111**, 325; (*g*) R. S. Reddy, J. S. Reddy, R. Kumar and P. Kumar, *J. Chem. Soc., Chem. Commun.*, 1992, 84; (*h*) P. S. Ragavan, V. Ramaswamy, T. T. Upadhya, A. Sudalai, A. V. Ramaswamy and S. Sivasankar, *J. Mol. Catal. A*, 1997, **122**, 75; (*i*) S. V. N. Raju, T. T. Upadhya, S. Ponatnam, T. Daniel and A. Sudalai, *Chem. Commun.*, 1996, 1969.

29 A. Corma, M. Iglesias and F. Sanchez, *Catal. Lett.*, 1996, **39**, 153.

30 M. Fraile, J. I. Garcia, B. Lazaro and J. Mayoral, *Chem. Commun.*, 1998, 1807.

31 F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, 1991, **11**, 173.

32 (*a*) M. Lakshmi Kantam, B. M. Choudary, Ch. Venkat Reddy, K. K. Rao and F. Figueras, *Chem. Commun.*, 1998, 1033; (*b*) B. M. Choudary, M. Lakshmi Kantam, B. Kavitha, Ch. Venkat Reddy, K. K. Rao and F. Figueras, *Tetrahedron Lett.*, 1998, **39**, 3555; (*c*) B. M. Choudary, M. Lakshmi Kantam, B. Bharathi and Ch. Venkat Reddy, *Synlett*, 1998, 1203; (*d*) P. S. Kumbhar, J. S. Valente, J. Lopez and F. Figueras, *Chem. Commun.*, 1998, 535; (*e*) B. Sels, D. De Vos, M. Buntinx, P. Frederic, A. K. Mesmaeker and P. A. Jacobs, *Nature*, 1999, 855; (*f*) B. M. Choudary, M. L. Kantam, A. Rahman, Ch. Venkat Reddy and K. K. Rao, *Angew. Chem., Int. Ed.*, 2001, **40**, 763.

33 B. M. Choudary, B. Bharathi, Ch. Venkat Reddy and M. Lakshmi Kantam, *Chem. Commun.*, 2001, 1736.

34 S. Miyata, *Clays Clay Miner.*, 1975, **23**, 369.

35 (*a*) M. H. Dickman and M. T. Pope, *Chem. Rev.*, 1994, **94**, 569; (*b*) R. Neumann and M. Gara, *J. Am, Chem. Soc.*, 1995, **117**, 5066.

36 D. Hoegaerts, B. F. Sels, D. E. Devos, F. Verport and P. A. Jacobs, *Catal. Today*, 2000, **60**, 209.

37 P. J. Kropp, G. W. Breton, J. D. Fields, J. C. Jung and B. R. Loomis, *J. Am. Chem. Soc.*, 2000, **122**, 4280.

38 J. B. Arterburn and S. L. Nelson, *J. Org. Chem.*, 1996, **61**, 2260.

39 J. Drabowicz, P. Lyzwa, M. Popielarczyk and M. Mikolajczyk, *Synthesis*, 1990, 937.