Peroxymolybdenum Complexes in Sulfide to Sulfone Oxidations

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Peroxymolybdenum complexes have been studied as reagents for the oxidation of sulfides to sulfones. The MoO₃·H₂O·HMPA complex is a useful reagent for the chemoselective oxidation of sulfides to sulfones, and hydrolytically and acid sensitive sulfones can be prepared using this reagent.

Peroxymolybdenum complexes are powerful oxidation reagents that have found wide application in the oxidation of variously functionalized organic molecules.¹ We have earlier reported that the peroxyxymolybdenum complex, oxodiperoxymolybdenum(aquao)hexamethyolphosphoric triamide (MoO₃·H₂O·HMPA) is a useful reagent for the oxidation of sulfides to sulfones,² and high selectivity for sulfide to sulfone oxidation has been demonstrated by the oxidation of an iodomethyl 2-pyrimidyl sulfide to the corresponding sulfone; m-chloroperbenzoic acid oxidation resulted in extensive evolution of iodine.² The usefulness of the molybdenum reagent for the oxidation of sulfoxides has subsequently been extended to dithioacetals, a class of compound which normally is difficult to oxidize to the bis(sulfone); orthodithioformates such as 2-alkoxybenzo-1,3-dithiokol can be oxidized to the corresponding alkoxylbis(sulfones) by MoO₃·H₂O·HMPA in dichloromethane at 0°C.³ The chemoselectivity indicated (vide supra) and the power to oxidize sulfides, which are not readily oxidizable by other reagents, led us to investigate further the potential of the MoO₃·H₂O·HMPA complex⁴ and other MoO₃ complexes as chemoselective oxidizing agents for sulfides (Scheme 1, Table 1).

Initial studies on the oxidation of the sulfides 1a and 1b (Table 1) to the sulfones 2a and 2b showed that the reaction rate was significantly higher for the MoO₃·H₂O·HMPA complex than for the MoO₃·pyridine·HMPA (MoOPH)® complex. Since the latter also suffered from low solubility in dichloromethane, which was the solvent used in the oxidations, its use was not further studied. Another peroxyxymolybdenum complex, [MoO₃·C₆H₅N(O)COO] Bu₄N⁺ (MoO₃PICO), has more recently been used in the oxidations of some sulfides and sulfoxides to the corresponding sulfoxides and sulfones.⁵ We found, however, that oxidation of dibenzyl sulfide (1a) with this complex gave a mixture of the corresponding sulfoxide and sulfone 2a in 14% and 57% yield, respectively, and the pyrimidinyl sulfide 1e resisted oxidation to its sulfone by this MoO₃ complex. These reactions indicate that MoO₃PICO is inferior to MoO₃·H₂O·HMPA in the oxidations of sulfides to sulfones (see Table 1). Further studies were therefore limited to the use of the MoO₃·H₂O·HMPA complex.

The oxidations were run at ambient temperature and the progress was monitored by TLC, the reaction time being 16–24 h. Dibenzyl and phenyl vinyl sulfides (1a and 1b) were oxidized to their sulfones 2a and 2b in yields comparable to the high yields from the m-chloroperbenzoic acid (MCPBA) oxidations (Table 1). The pyrimidine sulfone 2c was isolated in lower yield. The importance of the molybdenum peroxide reagent becomes apparent in acid-sensitive sulfones, and by the chemoselectivity exhibited by the reagent. Relevant examples are provided by the oxidation of the sulfides 1f and 1f to the sulfones 2f and 2f, respectively. With MCPBA under standard conditions, i.e., with basic aqueous work-up, the sulfones were isolated in lower yields, partly because of oxidations in the imidazole moiety, and partly because of the ready hydrolysis of the sulfone function in the electrophilic pyrimidine 2-position which is additionally activated by the 5-carbonyl group. Under anhydrous work-up conditions, however, the sulfone 2e could be isolated in 64% yield after oxidation with MCPBA. The product was contaminated with m-chlorobenzoic acid and MCPBA. The chemoselective oxidation with the MoO₃·H₂O·HMPA reagent, and the absence of water in the work-up (see the Experimental) prevented hydrolysis of the labile sulfonic group in 2e, and it was obtained in 78% yield. The water molecule contained in the Me-complex did not cause any problem in this context. The sulfone 2f is very labile and it could not be purified by

\[
\text{R}^1\text{S}^−\text{R}^2^−\overset{\text{MoO}_3\text{ complexes}}{\underset{\text{CH}_2\text{Cl}_2}{\longrightarrow}}\text{R}^1\text{−S}−\text{R}^2^−\overset{\text{O}}{\longrightarrow}
\]

\[
\begin{array}{c}
\text{Scheme 1.} \\
\end{array}
\]

R¹ = alkyl, aryl and heteroaryl
R² = alkyl, alkenyl and aryl

Table 1. Oxidation of the sulfides 1 to the sulfones 2 with MoO₃·H₂O·HMPA.

<table>
<thead>
<tr>
<th>Sulfide/ sulfone</th>
<th>R¹</th>
<th>R²</th>
<th>Yield of sulphone (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 a</td>
<td>CH₂Ph</td>
<td>CH₂Ph</td>
<td>83 (92)¹</td>
</tr>
<tr>
<td>b</td>
<td>Ph</td>
<td>CH=CH₂</td>
<td>80 (52)¹</td>
</tr>
<tr>
<td>c</td>
<td>5-Pyrimidin-2-Cl</td>
<td>Pr</td>
<td>55 (74)¹</td>
</tr>
<tr>
<td>d</td>
<td>2-Pyrimidinyl</td>
<td>CH₂Ph</td>
<td>48</td>
</tr>
<tr>
<td>e</td>
<td>Me</td>
<td>Me</td>
<td>78 (23)² (64)²³</td>
</tr>
<tr>
<td>f</td>
<td>Me</td>
<td>Me</td>
<td>56²</td>
</tr>
<tr>
<td>g</td>
<td>Ph</td>
<td>CH₂OCH₂Ph</td>
<td>88 (86)²</td>
</tr>
<tr>
<td>h</td>
<td>4-MeO₂C₆H₄</td>
<td>CH₂OCH₂Ph</td>
<td>71</td>
</tr>
<tr>
<td>i</td>
<td>4-NO₂C₆H₄</td>
<td>CH₂OCH₂Ph</td>
<td>43</td>
</tr>
<tr>
<td>j</td>
<td>2-Pyrimidinyl</td>
<td>CH₂Ph</td>
<td>0 (78)²</td>
</tr>
<tr>
<td>k</td>
<td>2-Pyrimidinyl</td>
<td>CH₂OCH₂Ph</td>
<td>0</td>
</tr>
<tr>
<td>l</td>
<td>5-Chl-2-pyrimidinyl-OCH₂</td>
<td>Ph</td>
<td>60</td>
</tr>
</tbody>
</table>

¹Yield in parentheses from MCPBA oxidation with aqueous basic work-up. ²Yield in parentheses from MCPBA oxidation with anhydrous work-up. ³The product was contaminated with m-chlorobenzoic acid and MCPBA. ⁴Calculated by ¹H NMR spectroscopy of the crude product.

column chromatography on silica gel without decomposition. ¹H NMR spectroscopy of the crude oxidation product, however, showed only one resonance (δ 3.41) in the region 2.8-4.0 ppm, which together with the mass spectrum confirmed the formation of the sulphone 2f. Indirect evidence for the sulphone 2f, was obtained by treatment of the crude reaction mixture with an excess of thiophenol and triethylamine, when the sulphone 3 was formed (Scheme 2). In the oxidation of the benzoxymethyl phenyl sulfides (1g-1h) to the sulfones 2g-2h the yields of the oxidation products decrease with an increase in the electron withdrawing effect of the para substituent in the phenyl ring (Table 1). Exchange of the phenyl ring for the highly π-electron deficient pyrimidine ring, gave no product corresponding to the sulphone 2j with MoO₃·H₂O·HMPA. In the case of the analogue 11 the sulfur atom is no longer attached directly to the pyrimidine ring, and the oxidation proceeded readily to the sulphone 2i. We reason that the oxidation of 1i and 1k proceeds to the sulphone 2j and 2k, since 1j is oxidized to the sulphone 2j in good yield by MCPBA (Table 1). Compounds 2j and 2k, however, are chemically unstable in the oxidation with MoO₃·H₂O·HMPA probably as a result of the activation of the methylene carbon from its ether oxygen. The methylene carbon is further attacked by the oxidation reagent and a hydroxy group is introduced (Scheme 2).

In the literature MoOPH is described as a reagent of choice for hydroxylation on activated carbon. Ketones, esters and cyanides having an enolizable α-methylene or methylene groups, after conversion into enolates, are hydroxylated by MoOPH to form α-hydroxy carbonyl com-

![Scheme 2](image-url)
pounds. Similarly, α-carbanions of aryl sulfones and nitro compounds undergo the hydroxylation reaction with MoOPH with concomitant elimination to the corresponding ketone.  

The pyrimidine ring is highly electron-withdrawing, and it seems likely that this property may be enhanced by complexation of a pyrimidine nitrogen with molybdenum species which have Lewis acid properties. The enolization is towards the sulfonyl group, and the attack on the enol by the molybdenum complex leads to α-hydroxylation (4). In a subsequent step the product should collapse to an ester and pyridine-2-sulfonic acid which may be further oxidized. This rationalization is supported by the finding that the reactions with the phenyl or benzoxymethyl sulfides (1i and 1k) required 2–3 equivalents of the peroxymolybdenum reagent before the starting material was consumed, and that the phenyl and benzyl esters (5a and 5b), respectively, were isolated.

**Experimental**

The mass spectra under electron impact conditions were recorded at 70 eV. Isobutane was used for chemical ionization (CI). The primary FAB beam was xenon atoms with energies of 8 keV. The liquid matrix was glycerol. The spectra are presented as m/z (rel. int.). The 1H NMR spectra were recorded at 60 MHz, 200 MHz or 300 MHz and the 13C NMR spectra at 22.5 MHz, 50 MHz or 75 MHz. The solvent was CDCl3. Dichloromethane was distilled from CaH2.

Compounds available by literature methods. Oxodiperoxymolybdenum(aqua)hexamethylphosphoric triamide. [Hexamethylphosphoric triamide (HMPA) should be handled with care as a suspected carcinogen]. Oxodiperoxymolybdenum(pyridine)hexamethylphosphoric triamide. [MoO2·C6H5N(O)COO]·Bu4N+. 2-Benzylsulfinylpyrimidine (1d). 10 Benzoyl methyl phenyl sulfide (1g).

**Oxidation of dibenzyl sulfide** by [MoO2·C6H5N(O)COO]·Bu4N+. [MoO2·C6H5N(O)COO]·Bu4N+ (1.42 g, 2.47 mmol) in dichloromethane (17 ml) was added to a solution of dibenzyl sulfide (0.21 g, 1 mmol) in dichloromethane (10 ml). After being stirred at ambient temperature for 24 h the reaction mixture was washed with water (3×10 ml). The aqueous phase was separated and extracted with dichloromethane (3×5 ml). The combined organic phases were washed with 1 M potassium carbonate (3×5 ml), dried (MgSO4) and evaporated. The products were separated by chromatography on silica. Dibenzyl sulfone eluted first with hexane–EtOAc 6:4, followed by dibenzyl sulfoxide, which was eluted with hexane–EtOAc 1:9; yields: dibenzyl sulfone (0.14 g, 57%) m.p. 152°C, lit.12 152°C, dibenzyl sulfoxide (0.033 g, 14%) m.p. 135–136°C, lit.13 135–136°C.

2-Chloro-5-propylsulfinylpyrimidine (1c). By a two-step reaction: (i) 5-Propylsulfonyl-2(1H)-pyrimidinone. 3-Dimethylamino-2-propylsulfonylacrylaldehyde (prepared analogously to literature14) (11.5 g, 66 mmol) and urea (8.0, 133 mmol) were added to sodium ethoxide (9.1 g, 133 mmol) in ethanol (100 ml). The mixture was refluxed for 6 h, the ethanol distilled off, water (100 ml) added, the pH brought to 7 with 2 M HCl, the mixture extracted with chloroform (3×50 ml) and the organic phase dried (MgSO4) and evaporated; yield 3.9 g (35%), m.p. 161–162°C (EtOAc). Anal. C15H11N2O: C, H. 1H NMR (60 MHz): δ 1.00, 1.60 and 2.72 (Pr), 8.45 (s, H-4 and H-6), 10.4 (br s, NH). MS: 171 (9), 170 (100, M), 141 (18), 137 (18), 128 (73), 113 (8), 100 (12), 86 (10), 84 (17).

(ii) 2-Chloro 5-propylsulfinylpyrimidine (1c). 5-Propylsulfonyl-2(1H)-pyrimidinone (2.0 g, 11.7 mmol) was dissolved in phosphorus oxychloride (50 ml). N,N-Dimethylaniline (1.42 g, 11.7 mmol) was added, the mixture heated under reflux for 2 h, the excess of phosphorus oxychloride distilled off, the residue poured onto crushed ice, the water phase extracted with chloroform (3×30 ml) and the organic phase dried (MgSO4) and evaporated. Purification by flash chromatography (EtOAc) gave the desired product; yield 1.43 g (65%), m.p. 25°C (sublimation 20°C/0.001 mm Hg). Anal. C15H11ClN2O: C, H. 1H NMR (60 MHz): δ 1.05, 1.70 and 2.90 (Pr), 8.60 (s, H-4 and H-6). 13C NMR (22.5 MHz): δ 13.11 (CH3), 22.32 (CH2CH3). 35.76 (SCH3), 131.91 (C-5), 159.21 (C-4 and C-6), 165.50 (C-2). MS: 190/188 (14/37, M), 161 (3), 159 (7), 148 (12), 146 (36), 118 (8), 71 (5), 43 (100).

5-(1-Methylimidazole-2-carbonyl)-2-methylsulfinylpyrimidine (1e) 15

5-(1-Methylimidazole-5-carbonyl)-2-methylsulfinylpyrimidine (1f) 15

Benzoxymethyl 4-methoxy carbonylphenyl sulfide (1h). Chloromethyl benzyl ether (3.7 g, 23.8 mmol) was added dropwise to a mixture of methyl 4-mercaptobenzoate16 (4.0 g, 23.8 mmol) and triethylamine (2.4 g, 23.8 mmol) in dichloromethane (100 ml) under N2 at 0°C and the reaction allowed to reach ambient temperature during 1 h. The mixture was diluted with dichloromethane (100 ml), washed with water (3×30 ml), dried (MgSO4), evaporated and the residue distilled; yield 6.1 g (90%), oil. The product was purified by flash chromatography (CH2Cl2). Anal. C19H17OS: C, H. 1H NMR (60 MHz): δ 3.80 (Me), 4.65 (CH3Ph), 5.08 (CH3), 7.30 (Ph), 7.4–7.6 and 7.9–8.1 (4 H, m, Ar). 13C NMR (22.5 MHz): δ 52.06 (CH3), 73.57 (OCH3), 69.99 (SCH3), 126.33, 127.96, 128.23, 128.56, 130.01, 136.84, 142.97 (2×Ar), 168.81 (CO). MS (FAB): 289 (100, M+H).

Benzoxymethyl 4-nitrophenyl sulfide (1i). Compound 1i was prepared as for 1h above from 4-nitrothiophenol (2.0 g, 13.0 mmol), chloromethyl benzyl ether (2.0 g, 13.0 mmol) and triethylamine (1.3 g, 13.0 mmol) in dichloro-
methane (50 ml); yield 3.4 g (94 %), oil. The product was purified by flash chromatography (CH₂Cl₂). Anal. C₇H₆NO₂S: C, H. ¹H NMR (60 MHz): δ 4.70 (CH₂Ph), 5.13 (CH₃), 7.39 (Ph), 7.5–7.7 and 8.1–8.2 (4 H, Ar). ¹³C NMR (22.5 MHz): δ 70.21 (SCH₂), 73.03 (OCH₃), 123.90, 127.74, 128.18, 128.56, 136.47, 145.78, 146.33 (2×Ar). MS (FAB): 276 (100, M+H).

2-Phenoxymethylsulfonylpyrimidine (1j). Compound 1j was prepared as for 1h above from 2-mercaptopyrimidine (0.39 g, 3.5 mmol), chloromethyl phenyl ether17 (0.5 g, 3.5 mmol) and triethylamine (0.35 g, 3.5 mmol) in dichloromethane (10 ml); yield 0.66 g (86 %), m.p. 46–48°C. Anal. C₁₀H₇NO₂S: C, H. ¹H NMR (300 MHz): δ 5.88 (SCH₂O), 6.9–7.0 and 7.2–7.3 (6 H, Ar + H-5), 8.51 (d, J 5 Hz, H-4 and H-6). ¹³C NMR (75 MHz): δ 68.59 (SCH₂O), 115.83 (C-5), 117.34, 121.96, 129.46 and 156.97 (Ar), 157.49 (C-4 and C-6), 169.85 (C-2), MS (FAB): 219 (60, M+H).

2-Benzoxymethylsulfonylpyrimidine (1k). Compound 1k was prepared as for 1h above from 2-mercaptopyrimidine (2.0 g, 17.8 mmol), chloromethyl benzyl ether (2.79 g, 17.8 mmol) and triethylamine (1.8 g, 17.8 mmol) in dichloromethane (50 ml); yield 2.59 g (63 %), oil. The product was purified by flash chromatography (hexane–EtOAc 3:2). Anal. C₁₂H₁₀N₂O₂S: H. Calc. C, 64.04 %; found 61.62 %. ¹H NMR (60 MHz): δ 4.60 (CH₂Ph), 5.20 (CH₃), 6.70 (t, J 5 Hz, H-5), 7.23 (Ph), 8.43 (d, J 5 Hz, H-4 and H-6). ¹³C NMR (75 MHz): δ 70.76, 71.17 (SCH₂OCH₂), 117.17 (C-5), 127.86, 128.21, 128.39, 137.07 (Ar), 157.43 (C-4 and C-6), 170.81 (C-2). MS (FAB): 233 (70, M+H).

5-Chloro-2-phenoxymethylsulfonylpyrimidine (II). Chloromethyl phenyl sulfide18 (2.67 g, 16.8 mmol) was added to a mixture of 5-chloro-2-pyridimidine19 (2.0 g, 15 mmol) and cesium carbonate (5.49 g, 16.8 mmol) in DMF (500 ml). The reaction mixture stirred at 60°C for 4 h, DMF evaporated at reduced pressure, water (100 ml) added, the mixture extracted with diethyl ether (3×50 ml) and the dried (MgSO₄) ether solution evaporated. The product was a mixture of 5- and the O-alkylated isomers. The latter was isolated by flash chromatography (PhMe); yield 0.8 g (21 %), m.p. 72–73°C. Anal. C₁₀H₇NO₂S: C, H. ¹H NMR (60 MHz): δ 5.75 (CH₂), 7.1–7.6 (5 H, m, Ph), 8.35 (s, H-4 and H-6).

General procedure for the oxidation to sulfoxones

Method A: oxidation with MoO₃·H₂O·HMPA. MoO₃·H₂O·HMPA (7.0 mmol) was added to a solution of the sulfide (5.0 mmol) in dry dichloromethane (30 ml) and the mixture was stirred at ambient temperature until TLC monitoring showed that the reaction was complete (usually 16–24 h). The organic phase was washed with water (30 ml), the water phase extracted with dichloromethane (2×20 ml), the combined organic phases washed with 10 % K₂CO₃ and the dried (MgSO₄) solution evaporated. The product was dissolved in diethyl ether, washed with water to remove any HMPA residue, dried and evaporated. In some cases the product was further purified by flash chromatography.

Method B: Oxidation with MCPBA. The oxidation with MCPBA was carried out under standard conditions in dichloromethane.²⁰

Dibenyl sulfone (2a). Yield (A) 0.97 g (83 %); (B) 1.07 g (92 %), m.p. 152°C (lit.21 152°C).

Phenyl vinyl sulfone (2b). Yield (A) 1.34 g (80 %); (B) 0.44 g (52 %), m.p. 68°C (lit.21 72°C).

2-Chloro-5-propylsulfonylpyrimidine (2c). Yield (A) 0.32 g (55 %); (B) 0.43 g (74 %), m.p. 112°C. Anal. C₁₀H₁₃N₂O₂S: C, H. ¹H NMR (300 MHz): δ 1.05, 1.84 and 3.20 (Pr), 9.08 (s, H-4 and H-6). ¹³C NMR (75 MHz): δ 12.61 (Me), 16.24 (CH₂CH₂Me), 58.39 (CH₂Et), 132.67 (C-5), 159.17 (C-4 and C-6), 165.50 (C-2). MS: 222/220 (0.2/0.7, M), 179 (2), 155 (2), 154 (2), 128 (6), 114 (8), 86 (6), 43 (100).

2-Benzylsulfonylpyrimidine (2d). Yield (A) 0.28 g (48 %), m.p. 92–93°C. Anal. C₁₁H₁₀N₂O₂S: C, H. ¹H NMR (200 MHz): δ 4.67 (CH₂), 7.1–7.2 (Ph), 7.45 (t, J 5 Hz, H-5), 8.80 (d, J 5 Hz, H-4 and H-6). ¹³C NMR (50 MHz): δ 56.84 (CH₂), 123.20 (C-5), 128.25, 128.31, 130.64, 137.10 (Ph), 158.00 (C-4 and C-6), 167.15 (C-2). MS: 234 (4, M), 170 (11), 169 (70), 168 (2), 167 (2), 117 (2), 91 (100).

5-(1-Methylimidazo-2-carbonyl)-2-methylsulfonylpyrimidine (2e). A solution of MoO₃·H₂O·HMPA (1.40 g, 3.8 mmol) in dichloromethane (20 ml) was added slowly to a solution of 5-(1-methylimidazo-2-carbonyl)-2-methylsulfonylpyrimidine (0.35 g, 1.5 mmol) in dichloromethane (20 ml) at 0°C. The mixture was stirred at ambient temperature for 15 h, filtered, the filtrate applied to a silica gel column and the column eluted with EtOAc–hexane 9:1 (flash). Evaporation of the eluted compound left 313 mg (78 %) of the oxidation product, m.p. 124°C. Anal. C₁₀H₁₀N₂O₂S: H. Calc. C 45.11 %; found C 45.74 %.

¹H NMR (300 MHz): δ 3.42 (SO₃Me), 4.15 (NMMe), 7.27 and 7.32 (2 H, s, imid.), 9.78 (s, H-4 and H-6). ¹³C NMR (75 MHz): δ 36.6, 39.4, 128.8 and 131.0 (imid-4.5), 132.6 (C-5), 142.1 (imid-2), 160.6 (C-4 and C-6), 167.2 (C-2), 178.1 (CO), IR (KBr): 1660, 1315 and 1120 cm⁻¹. MS: 266 (6, M), 265 (15), 188 (11), 187 (100), 160 (19), 159 (21), 149 (15), 109 (38), 81 (13).

5-(1-Methylimidazo-2-carbonyl)-2-methylsulfonylpyrimidine (2f). MoO₃·H₂O·HMPA (314 mg, 0.84 mmol) in dichloromethane (5 ml) was added dropwise at 0°C to a solution of 5-(1-methylimidazo-2-carbonyl)-2-methylsulfonylpyrimidine (80 mg, 0.34 mmol) in dichloromethane.
The mixture was stirred at ambient temperature for 24 h before it was filtered and evaporated. The crude product \(^1\)HNMR: \(\delta\) 3.41 (SO\(_2\)Me), 4.03 (NMe), 7.63 and 7.77 (2 H, s, imid.); 9.26 (s, H-4, H-6), which contained HMPA, was used without further purification in the synthesis of 5-(1-methylimidazole-5-carbonyl)-2-phenylsulfenylpyrimidine (3) (vide supra).

Benzyloxyethyl phenyl sulfone (2g). Yield (A) 0.99 g (88%); (B) 0.97 g (86%), m.p. 72 °C (lit.\(^{11}\) 68-71 °C).

Benzyloxyethyl 4-methoxyacarbonylphenyl sulfone (2h). Yield (A) 0.79 g (71%), m.p. 86-87 °C. Anal. C\(_{28}\)H\(_{24}\)O\(_3\)S: C, H. \(^1\)HNMR (300 MHz): \(\delta\) 3.98 (Me), 4.60 (CH\(_2\)Ph), 4.90 (CH\(_3\)), 7.2-7.4 (Ph), 8.0-8.1 and 8.2-8.3 (4 H, m, Ar). \(^13\)CNMR (75 MHz): \(\delta\) 52.54 (Me), 74.55 (OCH\(_2\)Ph), 84.52 (CH\(_3\)O), 128.13, 128.42, 128.53, 128.78, 130.13, 135.00, 135.49, 141.17 (Ar), 165.32 (CO). MS (FAB): 321 (20, M+H).

Benzyloxyethyl 4-nitrophenyl sulfone (2i). Yield (A) 0.24 g (43%), m.p. 114-115 °C. Anal. C\(_{28}\)H\(_{22}\)N\(_2\)O\(_5\): C, H. \(^1\)HNMR (200 MHz): \(\delta\) 4.55 (CH\(_2\)Ph), 4.85 (CH\(_2\)), 7.2-7.3 (Ph), 8.0-8.1 and 8.3-8.4 (4 H, m, Ar). \(^13\)CNMR (50 MHz): \(\delta\) 75.24 (OCH\(_3\)), 84.88 (SO\(_2\)CH\(_2\)), 124.83, 128.91, 129.30, 130.88, 136.22, 143.58, 146.21 (2×Ar). MS (CI): 308 (2, M+H), 120 (5), 91 (100), 76 (3), 65 (5), 590 (5).

2-Phenoxyethylsulfenylpyrimidine (2j). Yield (B) 0.9 g (78%), m.p. 78-79 °C. Anal. C\(_{21}\)H\(_{16}\)N\(_2\)O\(_5\): C, H. \(^1\)HNMR (300 MHz): \(\delta\) 5.61 (CH\(_3\)), 6.9-7.1 and 7.2-7.3 (Ph), 7.56 (t, J 5 Hz, H-5), 8.92 (d, J 5 Hz, H-4 and H-6). \(^13\)CNMR (75 MHz): \(\delta\) 79.89 (CH\(_3\)), 116.28 (C-5), 123.42, 124.12, 129.66 and 157.09 (Ar), 158.76 (C-4 and C-6), 164.56 (C-2). MS (EI): 250 (15, M), 187 (40), 185 (80), 169 (5), 158 (25), 157 (73), 107 (100).

Oxidations of 1j and 1k by Mo\(_6\)O\(_{19}\)-H\(_2\)O·HMPA. The standard procedure was used. TLC monitoring showed a substantial amount of starting material left after 12 h. A further equivalent of the molybdenum complex was therefore added. The reaction mixture was worked up after 24 h after which time the substrate was consumed. Work-up by the standard procedure led to the isolation of phenyl and benzylic formate (5a and 5b, respectively). These structures were confirmed by NMR, IR and by GLC using authentic samples of 5a and 5b for comparison.

5-Chloro-2-phenylsulfenylmethylpyrimidine (2l). Yield 0.27 g (60%), m.p. 144 °C. Anal. C\(_{22}\)H\(_{19}\)ClN\(_2\)O\(_5\): C, H. \(^1\)HNMR (300 MHz): \(\delta\) 5.59 (CH\(_3\)), 7.5-7.7 and 7.9-8.0 (Ph), 8.45 (s, H-4 and H-6). \(^13\)CNMR (75 MHz): \(\delta\) 79.22 (CH\(_2\)), 125.76 (C-5), 128.82, 129.13, 134.18, 137.07 (Ar), 157.45 (C-4 and C-6), 161.37 (CO). MS (CI): 288 (9), 287 (21, M+H), 286 (25), 285 (47, M+H), 269 (25), 254 (19), 253 (15), 145 (6), 143 (17), 125 (13), 77 (44).

References

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