Peroxymolybdenum Complexes in Sulfide to Sulfone Oxidations

Gunnar Keilen, Tore Benneche, Kristin Gaare and Kjell Undheim

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

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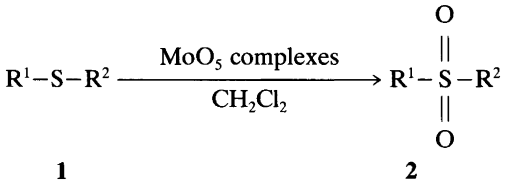
Peroxymolybdenum complexes have been studied as reagents for the oxidation of sulfides to sulfones. The $MoO_5 \cdot H_2O \cdot HMPA$ complex is a useful reagent for the chemoselective oxidation of sulfides to sulfones, and hydrolytically and acid sensitive sulfones can be prepared using this reagent.

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 peroxymolybdenum complex, oxodiperoxymolybdenum(aquo)hexamethylphosphoric triamide ($MoO_5 \cdot H_2O \cdot HMPA$) 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-pyrimidinyl 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 sulfides 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-dithioles can be oxidized to the corresponding alkoxybis(sulfones) by $MoO_5 \cdot H_2O \cdot HMPA$ 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 $MoO_5 \cdot H_2O \cdot HMPA$ complex[4] and other MoO_5 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 $MoO_5 \cdot H_2O \cdot HMPA$ complex than for the $MoO_5 \cdot$ pyridine $\cdot$ HMPA (MoOPH)[4b] 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 peroxymolybdenum complex, $[MoO_5 \cdot C_5H_4N(O)COO]^- Bu_4N^+$ (MoO_5PICO), has more recently been used in the oxidations of some sulfides and sulfoxides to the corresponding sulfoxides and sulfones.[5a] 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 MoO_5-complex. These reactions indicate that MoO_5PICO is inferior to $MoO_5 \cdot H_2O \cdot HMPA$ in the oxidations of sulfides to sulfones (see Table 1). Further studies were therefore limited to the use of the $MoO_5 \cdot H_2O \cdot HMPA$ 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 **1e** and **1f** to the sulfones **2e** 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 $MoO_5 \cdot H_2O \cdot HMPA$ 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 Mo-complex did not cause any problem in this context. The sulfone **2f** is very labile and it could not be purified by

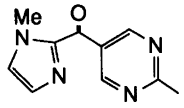
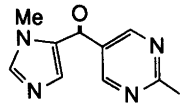


1 **2**

R^1 = alkyl, aryl and heteroaryl
R^2 = alkyl, alkenyl and aryl

Scheme 1.

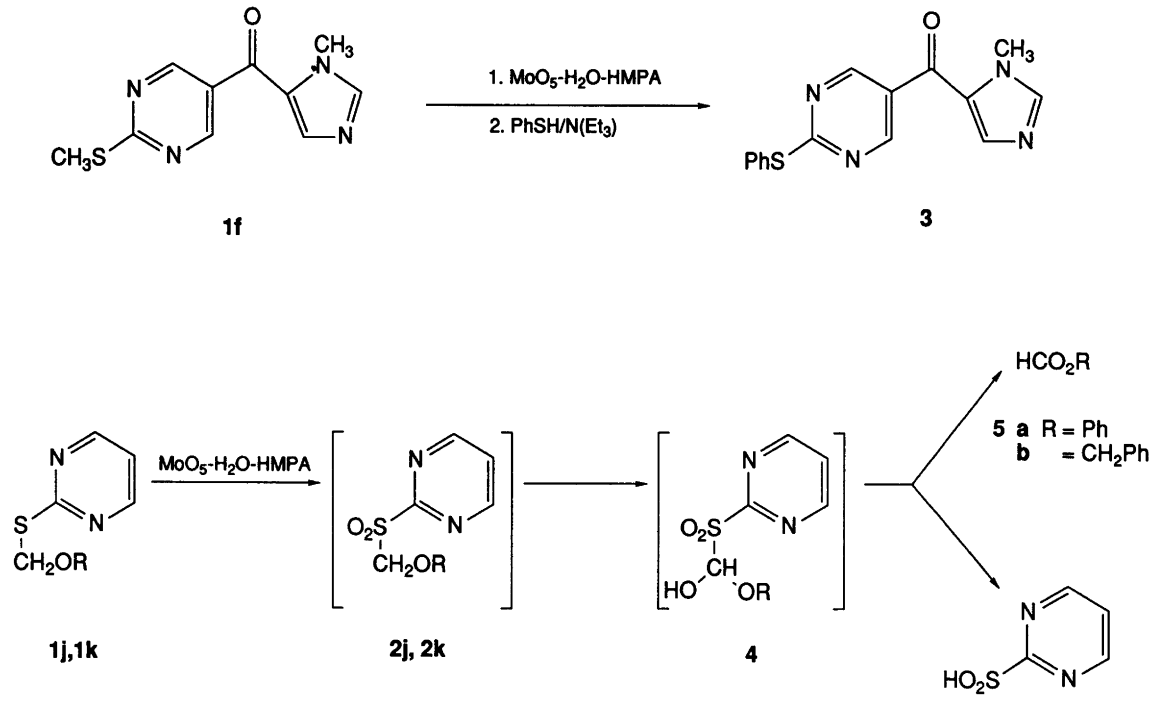
Table 1. Oxidation of the sulfides **1** to the sulfones **2** with $MoO_5 \cdot H_2O \cdot HMPA$.

Sulfide/ sulfone	R^1	R^2	Yield of sulfone (%)
1/2 a	CH_2Ph	CH_2Ph	83 (92)[a]
b	Ph	$CH{=}CH_2$	80 (52)[a]
c	5-Pyrimidinyl-2-Cl	Pr	55 (74)[a]
d	2-Pyrimidinyl	CH_2Ph	48
e		Me	78 (23)[a] (64)[b,c]
f		Me	56[d]
g	Ph	CH_2OCH_2Ph	88 (86)[a]
h	4-$MeO_2CC_6H_4$	CH_2OCH_2Ph	71
i	4-$NO_2C_6H_4$	CH_2OCH_2Ph	43
j	2-Pyrimidinyl	CH_2OPh	0 (78)[a]
k	2-Pyrimidinyl	CH_2OCH_2Ph	0
l	5-Cl-2-pyrimidinyl–OCH_2	Ph	60

[a]Yield in parentheses from MCPBA oxidation with aqueous basic work-up. [b]Yield in parentheses from MCPBA oxidation with anhydrous work-up. [c]The product was contaminated with *m*-chlorobenzoic acid and MCPBA. [d]Calculated by ^1H NMR spectrocopy of the crude product.

column chromatograpy 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 sulfone **2f**. Indirect evidence for the sulfone **2f**, was obtained by treatment of the crude reaction mixture with an excess of thiophenol and triethylamine, when the sulfide **3** was formed (Scheme 2). In the oxidation of the benzyloxymethyl 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 sulfone **2j** with $MoO_5 \cdot H_2O \cdot HMPA$. In the case of the analogue **1l** the sulfur atom is no longer attached directly to the pyrimidine ring, and the oxidation proceeded readily to the sulfone **2l**. We reason that the oxidation of **1i** and **1k** proceeds to the sulfone **2j** and **2k**, since **1j** is oxidized to the sulfone **2j** in good yield by MCPBA (Table 1). Compounds **2j** and **2k**, however, are chemically unstable in the oxidation with $MoO_5 \cdot H_2O \cdot HMPA$ 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-methine or methylene groups, after conversion into enolates, are hydroxylated by MoOPH to form α-hydroxycarbonyl com-



Scheme 2.

pounds.[6,7] Similarly, α-carbanions of aryl sulfones and nitro compounds undergo the hydroxylation reaction with MoOPH with concomitant elimination to the corresponding ketone.[8,9]

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-sulfinic acid which may be further oxidized. This rationalization is supported by the finding that the reactions with the phenyl or benzyloxymethyl 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 ^{1}H NMR spectra were recorded at 60 MHz, 200 MHz or 300 MHz and the ^{13}C NMR spectra at 22.5 MHz, 50 MHz or 75 MHz. The solvent was $CDCl_3$. Dichloromethane was distilled from CaH_2.

Compounds available by literature methods. Oxodiperoxymolybdenum(aqua)hexamethylphosphoric triamide.[4a] [Hexamethylphosphoric triamide (HMPA) should be handled with care as a suspected carcinogen]. Oxodiperoxymolybdenum(pyridine)hexamethylphosphoric triamide.[4a] $[MoO_5 \cdot C_5H_4N(O)COO^-]Bu_4N^+$.[5b] 2-Benzylsulfenylpyrimidine (**1d**).[10] Benzyloxymethyl phenyl sulfide (**1g**).[11]

Oxidation of dibenzyl sulfide by $[MoO_5 \cdot C_5H_4N(O)COO^-]Bu_4N^+$.[5b] $[MoO_5 \cdot C_5H_4N(O)COO^-]Bu_4N^+$ (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 ($MgSO_4$) 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-propylsulfenylpyrimidine (**1c**). By a two-step reaction: (i) *5-Propylsulfenyl-2(1H)-pyrimidinone.* 3-Dimethylamino-2-propylsulfenylacrylaldehyde (prepared analogously to literature[14]) (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 ($MgSO_4$) and evaporated; yield 3.9 g (35 %), m.p. 161–162 °C (EtOAc). Anal. $C_7H_{10}N_2OS$: C, H. ^{1}H 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-propylsulfenylpyrimidine* (**1c**). 5-Propylsulfenyl-2(1*H*)-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 ($MgSO_4$) 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 mmHg). Anal. $C_7H_9ClN_2S$: C, H. ^{1}H NMR (60 MHz): δ 1.05, 1.70 and 2.90 (Pr), 8.60 (s, H.4 and H-6). ^{13}C NMR (22.5 MHz): δ 13.11 (CH_3), 22.32 (CH_2CH_3), 35.76 (SCH_2), 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-methylsulfenylpyrimidine (**1e**)[15]

5-(1-Methylimidazole-5-carbonyl)-2-methylsulfenylpyrimidine (**1f**)[15]

Benzyloxymethyl 4-methoxycarbonylphenyl sulfide (**1h**). Chloromethyl benzyl ether (3.7 g, 23.8 mmol) was added dropwise to a mixture of methyl 4-mercaptobenzoate[16] (4.0 g, 23.8 mmol) and triethylamine (2.4 g, 23.8 mmol) in dichloromethane (100 ml) under N_2 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 ($MgSO_4$), evaporated and the residue distilled; yield 6.1 g (90 %), oil. The product was purified by flash chromatography (CH_2Cl_2). Anal. $C_{16}H_{16}O_3S$: C, H. ^{1}H NMR (60 MHz): δ 3.80 (Me), 4.65 (CH_2Ph), 5.08 (CH_2), 7.30 (Ph), 7.4–7.6 and 7.9–8.1 (4 H, m, Ar). ^{13}C NMR (22.5 MHz): δ 52.06 (CH_3), 73.57 (OCH_2), 69.99 (SCH_2), 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).

Benzyloxymethyl 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 (CH_2Cl_2). Anal. $C_{14}H_{13}NO_3S$: C, H. ^1H NMR (60 MHz): δ 4.70 (CH_2Ph), 5.13 (CH_2), 7.39 (Ph), 7.5–7.6 and 8.1–8.2 (4 H, Ar). ^{13}C NMR (22.5 MHz): δ 70.21 (SCH_2), 73.03 (OCH_2), 123.90, 127.74, 128.18, 128.56, 136.47, 145.78, 146.33 (2×Ar). MS (FAB): 276 (100, *M*+H).

2-Phenoxymethylsulfenylpyrimidine (**1j**). Compound **1j** was prepared as for **1h** above from 2-mercaptopyrimidine (0.39 g, 3.5 mmol), chloromethyl phenyl ether[17] (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. $C_{11}H_{10}N_2OS$: C, H. ^1H NMR (300 MHz): δ 5.88 (SCH_2O), 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). ^{13}C NMR (75 MHz): δ 68.59 (SCH_2O), 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-Benzyloxymethylsulfenylpyrimidine (**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. $C_{12}H_{12}N_2OS$: H. Calc. C, 64.04 %; found 61.62 %. ^1H NMR (60 MHz): δ 4.60 (CH_2Ph), 5.20 (CH_2), 6.70 (t, *J* 5 Hz, H-5), 7.23 (Ph), 8.43 (d, *J* 5 Hz, H-4 and H-6). ^{13}C NMR (75 MHz): δ 70.76, 71.17 (SCH_2OCH_2), 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-phenylsulfenylmethoxypyrimidine (**1l**). Chloromethyl phenyl sulfide[18] (2.67 g, 16.8 mmol) was added to a mixture of 5-chloro-2-pyrimidinone[19] (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 ($MgSO_4$) ether solution evaporated. The product was a mixture of *N*- and the *O*-alkylated isomers. The latter was isolated by flash chromatography (PhMe); yield 0.8 g (21 %), m.p. 72–73 °C. Anal. $C_{11}H_9ClN_2OS$: C, H. ^1H NMR (60 MHz): δ 5.75 (CH_2), 7.1–7.6 (5 H, m, Ph), 8.35 (s, H-4 and H-6).

General procedure for the oxidation to sulfones

Method A: oxidation with $MoO_5 \cdot H_2O \cdot HMPA$. $MoO_5 \cdot H_2O \cdot$ 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 % K_2CO_3 and the dried ($MgSO_4$) 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]

Dibenzyl sulfone (**2a**). Yield (A) 0.97 g (83 %); (B) 1.07 g (92 %), m.p. 152 °C (lit.[12] 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. $C_7H_9ClN_2O_2S$: C, H. ^1H NMR (300 MHz): δ 1.05, 1.84 and 3.20 (Pr), 9.08 (s, H-4 and H-6). ^{13}C NMR (75 MHz): δ 12.61 (Me), 16.24 (CH_2CH_2Me), 58.39 (CH_2Et), 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. $C_{11}H_{10}NO_2S$: C, H. ^1H NMR (200 MHz): δ 4.67 (CH_2), 7.1–7.2 (Ph), 7.45 (t, *J* 5 Hz, H-5), 8.80 (d, *J* 5 Hz, H-4 and H-6). ^{13}C NMR (50 MHz): δ 56.84 (CH_2), 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-Methylimidazole-2-carbonyl)-2-methylsulfonylpyrimidine (**2e**). A solution of $MoO_5 \cdot H_2O \cdot$ HMPA (1.40 g, 3.8 mmol) in dichloromethane (20 ml) was added slowly to a solution of 5-(1-methylimidazole-2-carbonyl)-2-methylsulfenylpyrimidine (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. $C_{10}H_{10}N_4O_3S$: H. Calc. C 45.11 %; found C 45.74 %. ^1H NMR (300 MHz): δ 3.42 (SO_2Me), 4.15 (NMe), 7.27 and 7.32 (2 H, s, imid.), 9.78 (s, H-4 and H-6). ^{13}C (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-Methylimidazole-5-carbonyl)-2-methylsulfonylpyrimidine (**2f**). $MoO_5 \cdot H_2O \cdot$ HMPA (314 mg, 0.84 mmol) in dichloromethane (5 ml) was added dropwise at 0 °C to a solution of 5-(1-methylimidazole-5-carbonyl)-2-methylsulfenylpyrimidine (80 mg, 0.34 mmol) in dichloromethane

(5 ml). The mixture was stirred at ambient temperature for 24 h before it was filtered and evaporated. The crude product [^{1}H NMR: δ 3.41 (SO_2Me), 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*).

Benzyloxymethyl phenyl sulfone (**2g**). Yield (A) 0.99 g (88 %); (B) 0.97 g (86 %), m.p. 72 °C (lit.[11] 68–71 °C).

Benzyloxymethyl 4-methoxycarbonylphenyl sulfone (**2h**). Yield (A) 0.79 g (71 %), m.p. 86–87 °C. Anal. $C_{16}H_{16}O_5S$: C, H. ^{1}H NMR (300 MHz): δ 3.98 (Me), 4.60 (CH_2Ph), 4.90 (CH_2), 7.2–7.4 (Ph), 8.0–8.1 and 8.2–8.3 (4 H, m, Ar). ^{13}C NMR (75 MHz): δ 52.54 (Me), 74.55 (OCH_2Ph), 84.52 (CH_2O), 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).

Benzyloxymethyl 4-nitrophenyl sulfone (**2i**). Yield (A) 0.24 g (43 %), m.p. 114–115 °C. Anal. $C_{14}H_{13}NO_5S$: C, H. ^{1}H NMR (200 MHz): δ 4.55 (CH_2Ph), 4.85 (CH_2), 7.2–7.3 (Ph), 8.0–8.1 and 8.3–8.4 (4 H, m, Ar). ^{13}C NMR (50 MHz): δ 75,24 (OCH_2), 84.88 (SO_2CH_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 (3).

2-Phenoxymethylsulfonylpyrimidine (**2j**). Yield (B) 0.9 g (78 %), m.p. 78–79 °C. Anal. $C_{11}H_{10}N_2O_3S$: C, H. ^{1}H NMR (300 MHz): δ 5.61 (CH_2), 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}C NMR (75 MHz): δ 79.89 (CH_2), 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* $MoO_5 \cdot H_2O \cdot HMPA$. 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 benzyl 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-phenylsulfonylmethoxypyrimidine (**2l**). Yield 0.27 g (60 %), m.p. 144 °C. Anal. $C_{11}H_9ClN_2O_3S$: C, H. ^{1}H NMR (300 MHz): δ 5.59 (CH_2), 7.5–7.7 and 7.9–8.0 (Ph), 8.45 (s, H-4 and H-6). ^{13}C NMR (75 MHz): δ 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).

5-(1-Methylimidazole-5-carbonyl)-2-phenylsulfenylpyrimidine (**3**). A mixture of thiophenol (80 mg, 0.73 mmol) and triethylamine (79 mg, 0.78 mmol) in dichloromethane was added to the crude product of **2f** (*vide supra*) (ca. 0.34 mmol) at 0 °C. The reaction mixture was stirred at ambient temperature for 18 h before it was filtered and the filtrate washed successively with 1 M sodium hydroxide (2×12 ml), water (2×12 ml) and brine (2×12 ml). The dried ($MgSO_4$) solution was evaporated and the product purified by column chromatography on silica gel (4 % methanol in ethyl acetate); yield 29 mg (28 %), m.p. 151–152 °C. Found: M^+, 296.0721. Calc. for $C_{15}H_{12}N_4OS$: *M*, 296.0732. ^{1}H NMR (200 MHz): δ 3.98 (s, MeN), 7.4–7.5 and 7.6–7.8 (Ph and imid.), 8.88 (s, H-4 and H-6). ^{13}C NMR (50 MHz): δ 35.29 (MeN), 128.03, 128.82, 129.92 (Ph), 130.33 (Ph), 135.79 (Ph), 141.50 (imid), 144.50 (imid) 158.06 (C-4, C-6), 177.22 (C-2), 181.20 (CO). MS: 296 (96, *M*), 295 (100, *M*−H), 267 (8), 215 (2), 210 (10), 187 (11), 184 (9), 135 (9), 109 (41), 107 (7), 81 (14), 77 (20).

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