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Oxidation of Chalcogenides using the Peroxo Complex of Molybdenum [MoO(O$_2$)$_2$(H$_2$O)(hmpa)], hmpa = hexamethylphosphoramide

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A oxidação de diversos selenetos, sulfetos, teluretos, selenóxidos, sulfóxidos e teluróxidos com o complexo [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] [hmpa = (Me$_2$N)$_3$PO] em tetraidrofurano a 65-70 °C, para produzir as correspondentes selenonas, sulfonas e teluronas em altos rendimentos, é relatada neste trabalho.

This work reports the oxidation of a variety of selenides, sulfides, tellurides, selenoxides, sulfoxides and telluroxides with [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] [hmpa = (Me$_2$N)$_3$PO] in tetrahydrofuran at 65-70 °C to produce the corresponding selenones, sulfones and tellurones in high yields.

Keywords: chalcogenides, sulfide, selenide, telluride, oxidation, [MoO(O$_2$)$_2$(H$_2$O)(hmpa)]

Introduction

The organic chemistry of sulfur, selenium and tellurium has been actively investigated.[1] The vast chemistry of sulfoxides and sulfones makes them useful synthons and intermediates for construction of chemically and biologically significant molecules.[2,3] The chemistry of selenones is of particular interest due to their thermal instability (fragmentation with olefin formation)[4] and their ability to stabilise adjacent anionic centres.[5] Although a plethora of reagents is known for oxidation of sulfides such as potassium permanganate,[6] *ortho*-iodoxybenzoic acid,[7] periodic acid or molecular bromine,[8] mercury(II) oxide-iodine[9] and benzeneseleninic acid,[10] the oxidation of selenides and tellurides[11] has received only a scant attention. Many of these procedures employ environmentally unfavourable reagents, solvents or catalysts. Formation of by-products and high cost are other drawbacks of reported procedures. Recently, a large number of transition metal compounds have been used as catalysts for oxidation of sulfides using H$_2$O$_2$.[12] One of the major problems with this method is the concomitant decomposition of H$_2$O$_2$, which therefore requires the use of a large excess of H$_2$O$_2$ to achieve quantitative conversion. As an example, the procedure reported by Brahami[13] for the oxidation of sulfide to sulfone requires 20 equivalents of H$_2$O$_2$ and 5 equivalent of ZrCl$_4$ *per* mole of sulfide. These results prompted us to

search for a new procedure for the oxidation of sulfides, selenides and tellurides.

Peroxo complexes of molybdenum,[14] although known for some time, have not been extensively studied as oxidants for organic substrates. So far, aqua(hexamethylphosphoramide) oxodiperoxomolybdenum(VI), [MoO(O$_2$)$_2$(H$_2$O)(hmpa)], has been used only for epoxidation of olefins,[15] oxidation of primary aromatic amines to corresponding nitroso derivatives[16] in the presence of H$_2$O$_2$ and for alkoylation of organopalladium compounds.[17] Our effort has been directed towards the extension of the chemistry of this peroxomolybdenum complex to other organic substrates. The oxidation chemistry of peroxometal complexes, namely Mo^{VI} and W^{VI} derivatives, closely resembles that of simple peroxides.[18] Therefore we decided to investigate the application of this Mo complex for oxidation of chalcogenides without the aid of hydrogen peroxide.

Results and Discussion

This is the first report on the oxygenation of sulfides, selenides, tellurides, sulfoxides, selenoxides and telluroxides to the corresponding sulfones, selenones and tellurones in high yields using [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] in tetrahydrofuran (THF) at 65-70 °C. Firstly, the oxidation of variety of diaryl, aryl alkyl and dialkyl selenides and selenoxides was carried out. The oxidation of the selenides was complete in 5-17 h as monitored by thin layer chromatography (TLC) using 1:3 molar

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ratio of substrate:Mo complex in dry THF at 65-70 °C, whereas selenoxides underwent complete oxidation in 5-8.5 h using 1:1.5 molar ratio of substrate:Mo complex in dry THF at reflux temperature. The optimum reaction conditions were identified using diphenyl selenide and diphenyl selenoxide as the model substrates. The reactions of diphenyl selenide were carried out in various solvents, e.g., acetonitrile, toluene, carbon tetrachloride, methanol, dimethyl formamide and 1,2-dichloroethane at ambient temperature and under reflux. No oxidation was observed in these solvents at ambient temperature, while only a small amount of diphenyl selenone was observed by TLC after 18-20 h of refluxing. THF was the solvent of choice for oxidation, as diphenyl selenide underwent complete oxidation in 14 h under reflux using 1:3 molar ratio of substrate to Mo complex. The reaction was not complete when a lower molar ratio of substrate to Mo complex was used. Selenoxides could be oxidized to the corresponding selenones using 1:1.5 molar ratio of substrate to Mo complex under similar conditions. It is clear from Table 1 that diaryl selenides and selenoxides undergo slower oxidation compared to dialkyl selenides and selenoxides. Aryl alkyl selenides did not undergo any oxidation. All results are listed in Table 1.

Subsequently, the oxidation of various diaryl, alkyl aryl, phenyl benzyl and dialkyl sulfides and sulfoxides to the corresponding sulfones was achieved successfully in high yields using [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] in THF at 65-70 °C. The oxidation of sulfides and sulfoxides was much faster as compared to selenides and selenoxides, and were completed in less then 3 h. Similarly to selenoxides (Table 1), sulfoxides required half the molar ratio of Mo complex (1:1.5) when compared to sulfides for complete oxidation. These results are listed in Table 2.

The scope of the reagent was extended for the oxidation of tellurides and telluroxides, for which not many oxidizing agents are known. We report herein a convenient procedure for oxidation of aromatic and aliphatic tellurides and telluroxides with [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] in THF at 65-70 °C to the corresponding tellurones. The oxidations were complete in 1.5-3 h. The reactions of tellurides and telluroxides were faster than those of selenides and selenoxides, but of similar order if compared to sulfides and sulfoxides. Telluroxides required half the molar ratio of complex when compared to tellurides. All results are listed in Table 3. The oxidations of chalcogenides are summarised in Scheme 1.

No deselenized, desulfurized or detellurized products were obtained in any of these reactions. No dehalogenation was observed in substrates containing halogen on phenyl ring. Oxidation of selenides, sulfides and tellurides to the corresponding dioxides has been observed to proceed *via*

Table 1. Oxidation of selenides and selenoxides with [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] in THF at 65-70 °C

Reaction number	Substrates (**1**)	Molar ratio [a] (S:Mo complex)	Time / h	Yield (**2**) / (%)
1	Diphenyl selenide (**1a**)	1:3	14	88
2	Di(*p*-tolyl)selenide (**1b**)	1:3	16	87
3	Di(*p*-chlorophenyl)selenide (**1c**)	1:3	15	91
4	Di(*p*-bromophenyl)selenide (**1d**)	1:3	16	83
5	Di(*p*-anisyl)selenide (**1e**)	1:3	17	87
6	Di(*n*-dodecyl)selenide (**1f**)	1:3	10	80
7	Di(*n*-butyl)selenide (**1g**)	1:3	8	78
8	Di(*n*-propyl)selenide (**1h**)	1:3	5	81
9	*p*-Tolyl *n*-propyl selenide (**1i**)	1:3	24	– [b]
10	*p*-Tolyl *n*-butyl selenide (**1j**)	1:3	18	– [b]
11	Diphenyl selenoxide (**1k**)	1:1.5	8.5	81
12	Di(*p*-tolyl)selenoxide (**1l**)	1:1.5	8	82
13	Di(*p*-chlorophenyl)selenoxide (**1m**)	1:1.5	7.5	82
14	Di(*p*-bromophenyl)selenoxide (**1n**)	1:1.5	8	78
15	Di(*p*-anisyl)selenoxide (**1o**)	1:1.5	7.5	79
16	Di(*n*-butyl)selenoxide (**1p**)	1:1.5	5	76
17	Di(*n*-propyl)selenoxide (**1q**)	1:1.5	5.5	81

[a] 5 mL of THF/ 0.1 g of substrate was used. [b] Starting material was recovered as such.

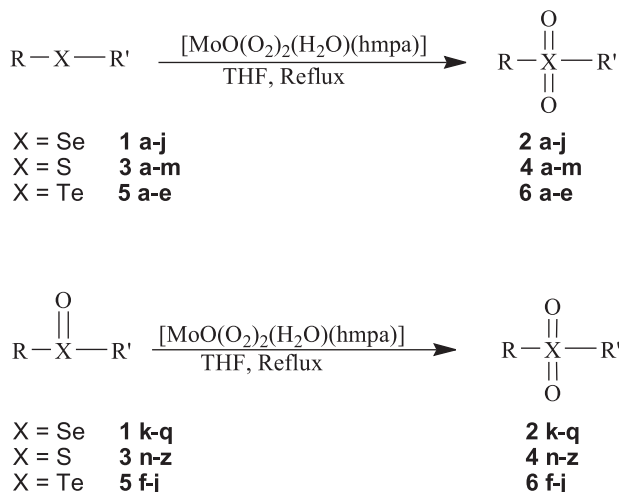**Table 2.** Oxidation of sulfides and sulfoxides with [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] in THF at 65-70 °C

Reaction number	Substrates (**3**)	Molar ratio (S:Mo complex)	Time / h	Yield (**4**) / (%)
18	Diphenyl sulfide (**3a**)	1:3	2	85
19	*p*-Tolylphenyl sulfide (**3b**)	1:3	1.5	93
20	*o*-Tolylphenyl sulfide (**3c**)	1:3	2.5	92
21	*p*-Anisylphenyl sulfide (**3d**)	1:3	2	96
22	*m*-Anisylphenyl sulfide (**3e**)	1:3	1.5	79
23	Phenyl *p*-chlorophenyl sulfide (**3f**)	1:3	1.5	91
24	Phenyl *m*-chlorophenyl sulfide (**3g**)	1:3	1.5	95
25	Phenyl *o*-chlorophenyl sulfide (**3h**)	1:3	2	87
26	Phenyl *p*-bromophenyl sulfide (**3i**)	1:3	6	80
27	Phenyl *n*-propyl sulfide (**3j**)	1:3	2.5	73
28	Phenyl methyl sulfide (**3k**)	1:3	2	81
29	Di(*n*-butyl)sulfide (**3l**)	1:3	2	86
30	Di(*n*-propyl)sulfide (**3m**)	1:3	1.5	76
31	Diphenyl sulfoxide (**3n**)	1:1.5	2	92
32	*p*-Tolylphenyl sulfoxide (**3o**)	1:1.5	1	89
33	*o*-Tolylphenyl sulfoxide (**3p**)	1:1.5	3	85
34	*p*-Anisylphenyl sulfoxide (**3q**)	1:1.5	2	90
35	*m*-Anisylphenyl sulfoxide (**3r**)	1:1.5	1	82
36	Phenyl *p*-chlorophenyl sulfoxide (**3s**)	1:1.5	1.5	89
37	Phenyl *m*-chlorophenyl sulfoxide (**3t**)	1:1.5	1.5	80
38	Phenyl *o*-chlorophenyl sulfoxide (**3u**)	1:1.5	3	76
39	Phenyl *p*-bromophenyl sufoxides (**3v**)	1:1.5	2.5	87
40	Phenyl *n*-propyl sulfoxide (**3w**)	1:1.5	1.5	78
41	Phenyl methyl sulfoxide (**3x**)	1:1.5	1.5	81
42	Di(*n*-butyl)sulfoxide (**3y**)	1:1.5	1	87
43	Di(*n*-propyl)sulfoxide (**3z**)	1:1.5	1	86

Table 3. Oxidation of tellurides and telluroxides with [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] in THF at 65-70 °C

Reaction number	Substrates (**5**)	Molar ratio (S:Mo complex)	Time / h	Yield (**6**) / (%)
44	Di(*p*-tolyl)telluride (**5a**)	1:3	2	82
45	Di(*p*-anisyl)telluride (**5b**)	1:3	3	80
46	Di(*p*-chlorophenyl)telluride (**5c**)	1:3	2.5	76
47	Di(*p*-bromophenyl)telluride (**5d**)	1:3	3	73
48	Di(*n*-butyl)telluride (**5e**)	1:3	1.5	74
49	Di(*p*-tolyl)telluroxide (**5f**)	1:1.5	2	83
50	Di(*p*-anisyl)telluroxide (**5g**)	1:1.5	2	79
51	Di(*p*-bromophenyl)telluroxide (**5h**)	1:1.5	2.5	77
52	Di(*p*-chlorophenyl)telluroxide (**5i**)	1:1.5	2.5	75
53	Di(*n*-butyl)telluroxide (**5j**)	1:1.5	1.5	76

the corresponding selenoxides, sulfoxides and telluroxides as monitored by TLC. However, controlled oxidation of sulfides, selenides and tellurides to corresponding monoxides could not be achieved selectively. The reaction is believed to proceed *via* 1,3-dipolar mechanism as proposed by Sajus and co-workers[15] for the oxidation of alkenes. The probable pathway for the oxidation of chalcogenides is shown in Scheme 2.

X = Se   **1 a-j**   **2 a-j**
X = S   **3 a-m**   **4 a-m**
X = Te   **5 a-e**   **6 a-e**

X = Se   **1 k-q**   **2 k-q**
X = S   **3 n-z**   **4 n-z**
X = Te   **5 f-j**   **6 f-j**

Scheme 1

Conclusions

We conclude that the oxidation of selenides, sulfides, tellurides, selenoxides, sulfoxides and telluroxides can be achieved using the $[MoO(O_2)_2(H_2O)(hmpa)]$ complex in THF at reflux temperature to give the corresponding selenones, sulfones and tellurones in high yields. The oxidations of sulfides, selenides and tellurides proceed *via* initial formation of selenoxides, sulfoxides and telluroxides respectively. The monoxides required half the molar ratio of reagent for oxidation.

Experimental

Materials and methods

All melting points were recorded on Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on Perkin Elmer FT-IR spectrum-2000. NMR spectra were recorded on FT-NMR model R-600 Hitachi (60 MHz) with TMS as internal standard. The products were identified by TLC, melting point determination (mp), IR and NMR

spectra. THF (Thomas Baker) was used in all reactions after distillation. The $[MoO(O_2)_2(H_2O)(hmpa)]$ complex was prepared by addition of H_2O_2 and HMPA to MoO_3.[19] MoO_3 (Thomas Baker), H_2O_2 (30%, E. Merck) and HMPA (Spectrochem) were used as such. The starting selenides,[20-22] selenoxides,[21,23,24] sulfides,[25-27] sulfoxides,[28] tellurides[29] and telluroxides[30] were prepared by reported procedures.

General procedure for the oxidation of selenides, sulfides and tellurides

In a typical reaction, a 25 mL round-bottomed flask was mounted over a magnetic stirrer and fitted with a reflux condenser and a $CaCl_2$ guard tube. Diphenyl selenide (0.1 g, 0.429 mmol) was then dissolved in 5 mL of dry THF. $[MoO(O_2)_2(H_2O)(hmpa)]$ (0.48 g, 1.288 mmol) was added and the reaction mixture was refluxed with vigorous stirring. The progress of the reaction was monitored by disappearance of diphenyl selenide on TLC by using petroleum ether: ethyl acetate (70:30, v/v) as eluent. The reaction was found to be complete after 14 h of reflux. The reaction mixture was cooled to room temperature and diluted with water (10 mL). The product was isolated by extraction with ethyl acetate (3×10 mL). The combined ethyl acetate extract was washed with water (2×10 mL) and dried over anhydrous $MgSO_4$. After decanting, the solvent was removed on a rotavapour. The product was purified by column chromatography (silica gel 100-200 mesh) using petroleum ether: ethyl acetate as eluent. The white solid obtained was identified to be diphenyl selenone (0.1 g, 88%) by mp 153-154 °C (lit. 155-156 °C)[24] and superimposable IR spectra.

General procedure for the oxidation for oxidation of selenoxides, sulfoxides and telluroxides

In a typical reaction, a 25 mL round-bottomed flask was mounted over a magnetic stirrer and fitted with a reflux condenser and a $CaCl_2$ guard tube. Di(*n*-butyl)sulfoxide
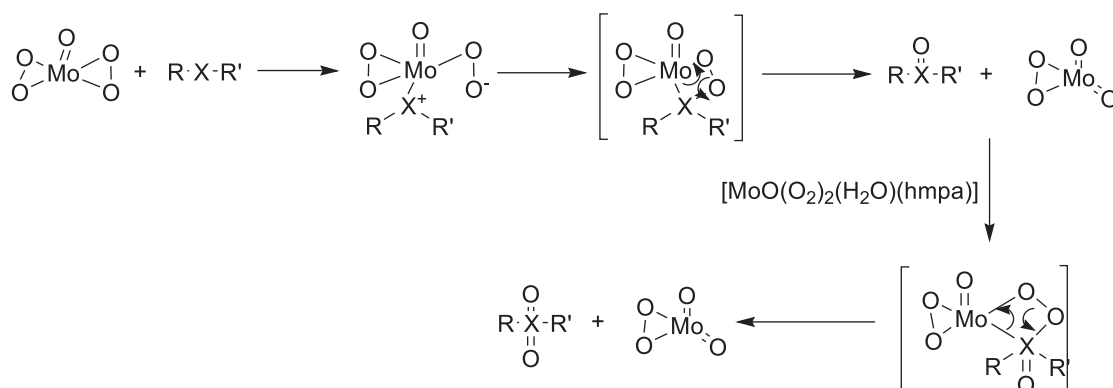
Scheme 2

(0.1 g, 0.617 mmol) was then dissolved in 5 mL of dry THF. [MoO(O$_2$)$_2$(H$_2$O)(hmpa)] (0.34 g, 0.926 mmol) was added and the reaction mixture was refluxed with vigorous stirring. The progress of the reaction was monitored by disappearance of the starting material on TLC by using petroleum ether:ethyl acetate (70:30, v/v) as eluent. After the completion, the reaction was worked up as above. The isolated product was identified by mp 42 °C (lit. 44 °C),[31] NMR and IR spectra as di(*n*-butyl)sulfone (0.096 g, 87%).

Selected spectral data

Diphenyl selenone 2a

IR (KBr) v$_{max}$/ cm^{-1}: 1574, 1460, 960 (s); ^{1}H-NMR (CDCl$_3$, 60 MHz, ppm): δ 7.0-7.4 (m, 10H, Ar-H); ^{13}C-NMR (CDCl$_3$, 300 MHz, ppm): δ 127.39, 129.4, 131.2, 133.05.

Di(n-butyl)sulfone 4y

IR (KBr) v$_{max}$/ cm^{-1}: 1448, 1309, 1155 (s); ^{1}H-NMR (CDCl$_3$, 60 MHz, ppm): δ 0.97 (t, 6H, CH$_3$), 1.48 (m, 4H, -C$\underline{H}_2$-CH$_3$), 1.82 (m, 4H, -CH$_2$-), 2.97 (t, 4H, -CH$_2$-S-); ^{13}C-NMR (CDCl$_3$, 300 MHz, ppm): δ 13.41 (CH$_3$), 21.63 (-C$\underline{H}_2$-CH$_3$) , 23.74 (-CH$_2$-), 52.29 (-CH$_2$-S-).

Di(p-anisyl)tellurone 6b

IR (KBr) v$_{max}$/ cm^{-1}: 1490 (s), 1253 (s), 1177, 1065, 699, 587; ^{1}H-NMR (CDCl$_3$, 60 MHz, ppm): δ 3.8 (s, 6H, -OCH$_3$), 7.0-7.8 (m, 8H, Ar-H); ^{13}C-NMR (CDCl$_3$, 300 MHz, ppm): δ 55.09 (-OC$\underline{H}_3$), 104.25, 115.33, 139.66, 159.61.

Acknowledgments

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