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Deoxygenation of sulfoxides, selenoxides, telluroxides, sulfones, selenones and tellurones with Mg–MeOH

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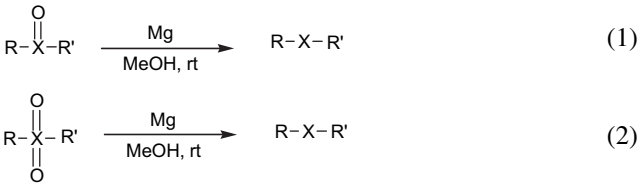
Abstract—The deoxygenation of a variety of sulfoxides, selenoxides, telluroxides, sulfones, selenones and tellurones has been reported with Mg–MeOH at room temperature in nearly quantitative yields. The deoxygenation is proposed to proceed by SET from Mg to the substrate.

1. Introduction

Recently Mg–MeOH has evoked considerable interest as an inexpensive and efficient reagent for a variety of organic transformations.[1] The dissolving metal reducing system generated by this reagent combination provides a convenient electron transfer/protic source for the reduction of C–C double bonds and triple bonds attached to esters, nitriles, amides and other carbonyls,[1] reduction of azides,[2] reductive coupling of nitroarenes,[3] dehalogenation of bromides and iodides,[4] reduction of aromatic carbonyl compounds,[5] desulfonylation reactions of sulfones,[6] deoxygenation of *N*-oxides,[7] and reductive cleavages and cyclizations.[1] In view of its diverse role as a reducing reagent, we decided to investigate the deoxygenation of sulfoxides, selenoxides, telluroxides, sulfones, selenones and tellurones. Though deoxygenation of sulfoxides[8] is well known, deoxygenation of selenoxides[8a,9] and telluroxides[9c] has received only scant attention. Sulfones are reported to undergo desulfonylation,[6] while deoxygenation of selenones and tellurones is not known.

2. Results and discussion

This is the first report on the deoxygenation of a variety of sulfoxides, selenoxides, telluroxides, sulfones, selenones and tellurones, to give the corresponding organo chalcogenides using Mg–MeOH at ambient temperature. The reactions have been performed with different sulfoxides, selenoxides, telluroxides, sulfones, selenones and tellurones, and the deoxygenated products were obtained in high yields (Eqs. 1 and 2). Reactions of all substrates were carried out by varying the molar ratios of substrate to magnesium to optimize the molar ratios for quantitative conversions. The reactions were induced by the addition of 1–2 crystals of iodine. The induction times and hence the times for completion of reactions were longer in the absence of iodine but did not affect the products. No deoxygenations were observed with magnesium in tetrahydrofuran or ethanol using diphenyl sulfoxide as a model substrate. These results are summarized in Tables 1 and 2.



The progress of the reactions was monitored by thin layer chromatography and the products were obtained by a simple work-up procedure. Dialkyl and phenyl alkyl sulfoxides and sulfones were resistant to deoxygenation probably because the α-hydrogens are more acidic and can be readily abstracted by the magnesium methoxide formed in the reaction, rather than undergoing electron transfer from magnesium. However, benzyl phenyl sulfoxide and sulfone did undergo deoxygenation under these conditions. Phenyl sulfone, which has been reported to undergo desulfonylation,[6] also underwent deoxygenation under our reaction conditions. It is also worth noting that all classes of selenoxides and selenones (diaryl, aryl alkyl and dialkyl) were deoxygenated successfully. Telluroxides and tellurones required higher molar ratios of magnesium and longer reaction times for complete deoxygenation compared to the sulfur and

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Table 1. Reactions of sulfoxides, selenoxides and telluroxides with Mg–MeOH

Entry	Substrate 	S:Mg	Time (h)	Yields (%)[a] R–X–R′	Obsd mp (lit. mp) (°C)
1	Diphenyl sulfoxide	1:10	1.5	78[17]	—
2	Benzyl phenyl sulfoxide	1:10	2	75[17]	46 (44)
3	*m*-Chlorophenyl phenyl sulfoxide	1:20	3	82[17]	—
4	*p*-Bromophenyl phenyl sulfoxide	1:20	3	80[17]	—
5	Phenyl *m*-tolyl sulfoxide	1:20	3	80[17]	—
6	Phenyl *p*-tolyl sulfoxide	1:20	3	81[17]	—
7	*p*-Anisyl phenyl sulfoxide	1:20	3	82[17]	—
8	*n*-Propyl phenyl sulfoxide	1:20	24	—[b]	—
9	Diphenyl selenoxide	1:20	2	80[18]	—
10	Di-*p*-tolyl selenoxide	1:20	3	82[18]	68–69 (69)
11	Di-*p*-anisyl selenoxide	1:20	3.5	82[18]	54–55 (55–56)
12	Di-*p*-bromophenyl selenoxide	1:20	3.5	82[18]	112 (114–115)
13	*n*-Propyl *p*-tolyl selenoxide	1:20	3	70[18]	—
14	*n*-Propyl phenyl selenoxide	1:20	3	71[18]	—
15	Di-*n*-butyl selenoxide	1:20	3	70[18]	—
16	Di-*p*-chlorophenyl telluroxide	1:25	3	87[19]	90–91 (93–94)
17	Di-*p*-anisyl telluroxide	1:25	5	82[19]	55 (54–55)
18	Di-*p*-tolyl telluroxide	1:25	5	82[19]	64–65 (67)
19	Di-*n*-butyl telluroxide	1:30	24	75[19]	—
20	Methyl phenyl telluroxide	1:30	4	73[19]	—

[a] Isolated yields.
[b] No reaction.

selenium analogues, probably due to their higher metallic character. No desulfurized, deselenized or detellurized products were obtained in these reactions. The deoxygenation of sulfones, selenones and tellurones proceeds via the corresponding sulfoxides, selenoxides and telluroxides as confirmed by monitoring the progress of the reaction with lower ratios of magnesium. In all cases, the halogen group attached to the aryl unit was unaffected. Mg reacts very quickly with MeOH and, therefore, an excess of Mg is required for completion of reactions.

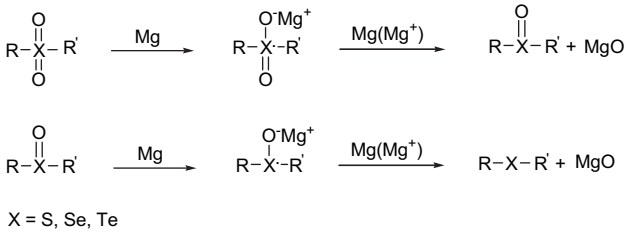
Reduction of these substrates with magnesium methoxide formed in situ, in a similar fashion to a *Meerwein–Ponndorff–Verley* reduction, has been ruled out since diphenyl sulfoxide and diphenyl sulfone did not undergo any reaction with preformed magnesium methoxide in methanol. We propose that the deoxygenations are proceeding via SET from magnesium to the LUMO of R_2XO_2 (X=S, Se, Te) to give a radical anion, which accepts another electron followed by loss of magnesium oxide to give $R_2X{=}O$, which undergo subsequent rapid deoxygenation to give the corresponding

Table 2. Reactions of sulfones, selenones and tellurones with Mg–MeOH

Entry	Substrate 	S:Mg	Time (h)	Yields (%)[a] R–X–R′	Obsd mp (lit. mp) (°C)
1	Diphenyl sulfone	1:20	1.5	82[17]	—
2	Phenyl *p*-tolyl sulfone	1:20	3	82[17]	—
3	*p*-Anisyl phenyl sulfone	1:20	3	83[17]	—
4	*p*-Bromophenyl phenyl sulfone	1:20	2.5	75[17]	—
5	Phenyl-*m*-tolyl sulfone	1:20	3	80[17]	—
6	*m*-Chlorophenyl phenyl sulfone	1:20	3	80[17]	—
7	Benzyl phenyl sulfone	1:20	3	83[17]	46 (44)
8	*n*-Propyl phenyl sulfone	1:20	24	—[b]	—
9	Diphenyl selenone	1:20	1.5	78[18]	—
10	Di-*p*-chlorophenyl selenone	1:20	3.5	86[18]	95–96 (95–96)
11	Di-*p*-bromophenyl selenone	1:20	4	90[18]	112 (114–115)
12	Di-*p*-tolyl selenone	1:20	3.5	87[18]	68–69 (69)
13	Di-*p*-anisyl selenone	1:20	4	82[18]	54–55 (55–56)
14	*n*-Propyl-*p*-tolyl selenone	1:25	4	82[18]	—
15	*n*-Propyl phenyl selenone	1:25	4	82[18]	—
16	*n*-Butyl phenyl selenone	1:25	4	82[18]	—
17	Di-*n*-butyl selenone	1:25	4	65[18]	—
18	Di-*p*-chlorophenyl tellurone	1:35	5	85[19]	90–91 (93–94)
19	Di-*p*-bromophenyl tellurone	1:35	5	88[19]	119 (120–121)
20	Di-*p*-anisyl tellurone	1:35	5	88[19]	55 (54–55)
21	Di-*p*-tolyl tellurone	1:35	5	88[19]	64–65 (67)
22	Di-*n*-butyl tellurone	1:35	5	58[19]	—
23	Methyl phenyl tellurone	1:35	5	78[19]	—

[a] Isolated yields.
[b] No reaction.

chalcogenides (Scheme 1). The deoxygenation of sulfoxides via free radical processes has already been reported.[8f–h] The deoxygenation of diphenyl sulfoxide and diphenyl sulfone was completely inhibited when the reaction was carried out by bubbling oxygen into the reaction mixture or in presence of *p*-dinitrobenzene, as expected.



Scheme 1.

We conclude that magnesium–methanol provides a convenient, mild and inexpensive method for the deoxygenation of sulfoxides, selenoxides, telluroxides, sulfones, selenones and tellurones to the corresponding chalcogenides at ambient temperature. It is an inexpensive and environmentally benign reagent compared to other reagents known for these deoxygenations, such as SmI_2, WCl_6, Lawesson's reagent and $NaBH_4$–I_2. None of these can deoxygenate all the mono- and dioxides of chalcogenides.

3. Experimental

3.1. General

Melting points were determined on a Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on Perkin Elmer FTIR Spectrum-2000. ^{1}H NMR spectra were recorded on FT-NMR model R-600 Hitachi (60 MHz) with TMS as the internal standard. Methanol (Speckpure), resublimed iodine (E. Merck) and magnesium turnings (S.D. Fine) were used in all the reactions. Methanol was dried by the published procedure.[10] Magnesium turnings were washed with 1% hydrochloric acid, water and acetone and finally dried. The starting sulfoxides,[11] sulfones,[12] tellurones[13] and selenones[13] were prepared by the reported procedures. Synthesis of selenoxides involved two-step preparations: (1) bromine addition to selenides to give selenide dibromides[14] and (2) alkaline hydrolysis of selenide dibromides to give selenoxides.[15] Telluroxides were prepared by a similar route to that reported previously.[16]

3.2. General procedures for deoxygenations

3.2.1. Diphenyl sulfoxide. In a typical procedure, a 50 mL round-bottomed flask, fitted with a reflux condenser and a $CaCl_2$ guard tube, was mounted over a magnetic stirrer. A mixture of diphenyl sulfoxide (0.1 g, 0.495 mmol), magnesium turnings (0.118 g, 4.95 mmol) and dry methanol (10 mL) was added. One or two crystals of iodine were added while stirring the contents magnetically at room temperature. A vigorous reaction ensued after ~15 min. The progress of the reaction was monitored by TLC using petroleum ether–ethyl acetate (85:15) as eluent. The starting material disappeared completely after 1.5 h. After completion, the reaction was quenched with the minimum volume of satd ammonium chloride solution and extracted with ether (3×10 mL). The combined extract was washed with satd sodium thiosulfate, dried over anhyd sodium sulfate and concentrated on a Buchi rotavapour to give a crude, which was purified by column chromatography on a silica gel (100–200 mesh) column (1×10 cm) using petroleum ether as eluent to give a pale yellow liquid, which was identified as diphenyl sulfide (0.072 g, 78%). IR (neat) 3059.52, 1580.26, 1475.90, 1439.71, 1080.74, 1024.14, 738.30, 689.96 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0 (s, 10H).

3.2.2. *n*-Propyl *p*-tolyl selenoxide. Reaction of *n*-propyl *p*-tolyl selenoxide (0.1 g, 0.4652 mmol) was carried out by the above procedure with magnesium (0.1959 g, 8.164 mmol). The product *n*-propyl *p*-tolyl selenide was obtained as golden yellow oil (0.061 g, 70%). IR (neat) 3018.26, 2919.43, 1486.97, 1013.91, 800.37, 480.80 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.9 (d, J=9 Hz, 2H), 7.2 (d, J=9 Hz, 2H), 3.5 (d, J=6 Hz, 2H), 2.4 (s, 3H), 1.6 (m, 2H), 1.0 (t, J=6 Hz, 3H).

3.2.3. Di-*n*-butyl telluroxide. Reaction of di-*n*-butyl telluroxide (0.1 g, 0.3891 mmol) was carried out by the above procedure with magnesium (0.2801 g, 11.673 mmol). The product di-*n*-butyl telluride was obtained as golden yellow oil (0.071 g, 75%). IR (neat) 2957.84, 2925.26, 1461.96, 1377.41, 1246.47, 1159.47, 886.32, 724.70 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.6 (t, J=6 Hz, 4H), 1.3–1.9 (m, 8H), 1.0 (t, J=6 Hz, 6H).

3.2.4. Phenyl *p*-tolyl sulfone. Reaction of phenyl *p*-tolyl sulfone (0.1 g, 0.431 mmol) was carried out by the above procedure with magnesium (0.2068 g, 8.62 mmol). The product phenyl *p*-tolyl sulfide was obtained as pale yellow oil (0.071 g, 82%). IR (neat) 3040.38, 2924.82, 1585.83, 1485.35, 1066.38, 938.46, 883.39, 809.15, 483.76 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.0 (s, 4H), 7.1 (s, 5H), 2.2 (s, 3H).

3.2.5. Di-*n*-butyl selenone. Reaction of di-*n*-butyl selenone (0.1 g, 0.4386 mmol) was carried out by the above procedure with magnesium (0.2631 g, 10.965 mmol). The product di-*n*-butyl selenide was obtained as colourless liquid (0.056 g, 65%). IR (neat) 2958.49, 2928.18, 1463.87, 1378.37, 1257.79, 1194.74, 902.29, 737.91 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.5 (t, J=6 Hz, 4H), 1.3–1.9 (m, 8H), 1.0 (t, J=6 Hz, 6H).

3.2.6. Di-*p*-anisyl tellurone. Reaction of di-*p*-anisyl tellurone (0.1 g, 0.2681 mmol) was carried out by the above procedure with magnesium (0.2252 g, 9.383 mmol). The product di-*p*-anisyl telluride was obtained as creamish solid (0.081 g, 88%), mp 55 °C (lit.[19] 54–55 °C). IR (KBr) 3001.08, 2936.94, 2835.60, 1586.09, 1487.95, 1283.66, 1245.46, 1176.57, 1029.93, 822.08, 587.36, 516.52 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.2 (d, J=9 Hz, 4H), 8.0 (d, J=9 Hz, 4H), 3.9 (s, 6H).

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References and notes

1. Lee, G. H.; Youn, I. K.; Choi, E. B.; Lee, H. K.; Yon, G. H.; Yang, H. C.; Pak, C. S. *Curr. Org. Chem.* **2004**, *8*, 1263.
2. Maiti, S. N.; Spevak, P.; Reddy, A. V. N. *Synth. Commun.* **1988**, *18*, 1201.
3. Khurana, J. M.; Ray, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 407.
4. (a) Hutchins, R. O.; Suchismita; Zipkin, R. E.; Taffer, I. M. *Synth. Commun.* **1989**, *19*, 1519; (b) Khurana, J. M.; Gogia, A.; Bankhwal, R. K. *Synth. Commun.* **1997**, *27*, 1801.
5. Khurana, J. M.; Bansal, G.; Kukreja, G.; Pandey, R. R. *Monatsh. Chem.* **2003**, *134*, 1365.
6. (a) Brown, A. C.; Carpino, L. A. *J. Org. Chem.* **1985**, *50*, 1749; (b) Lee, G. Y.; Lee, H. K.; Choi, E. B.; Kim, B. T.; Pak, C. S. *Tetrahedron Lett.* **1995**, *36*, 5607; (c) Lee, G. H.; Choi, E. B.; Lee, E.; Pak, C. S. *Tetrahedron Lett.* **1993**, *34*, 4541.
7. Hahn, W. E.; Lesiak, J. *Pol. J. Chem.* **1985**, *59*, 827.
8. (a) Khurana, J. M.; Ray, A.; Singh, S. *Tetrahedron Lett.* **1998**, *39*, 3829; (b) Karimi, B.; Zareyee, D. *Synthesis* **2003**, 1875; (c) Poor, N. I.; Firouzabadi, H.; Shaterian, H. R. *J. Org. Chem.* **2002**, *67*, 2826; (d) Karimi, B.; Zareyee, D. *Synthesis* **2003**, 335; (e) Posner, G. H.; Tang, P. W. *J. Org. Chem.* **1978**, *43*, 4131; (f) Madesclaire, M. *Tetrahedron* **1988**, *44*, 6537; (g) Barstch, H.; Erker, T. *Tetrahedron Lett.* **1992**, *33*, 1997; (h) Balicki, R. *Synthesis* **1991**, 155.
9. (a) Stratakis, M.; Rabalakos, C.; Soflkiti, N. *Tetrahedron Lett.* **2003**, *44*, 349; (b) Engman, L.; Persson, J. *Synth. Commun.* **1993**, *23*, 445; (c) Lang, E. S.; Comasseto, J. V. *Synth. Commun.* **1988**, *18*, 301; (d) Procter, D. J.; Thornton-Pett, M.; Rayner, C. M. *Tetrahedron* **1996**, *52*, 1841.
10. Vogel, A. I. *Textbook of Practical Organic Chemistry*, 4th ed.; ELBS: Oxford, 1987; p 169.
11. (a) Leandri, G.; Mangini, A.; Passerini, R. *J. Chem. Soc.* **1957**, 1386; (b) Harville, R.; Reed, S. F. *J. Org. Chem.* **1968**, *33*, 3976; (c) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282.
12. Khurana, J. M.; Panda, A.; Gogia, A.; Ray, A. *Org. Prep. Proced. Int.* **1996**, *28*, 234.
13. Khurana, J. M.; Kandpal, B. M.; Chauhan, Y. K. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 1369.
14. (a) Bird, M. L.; Challenger, F. *J. Chem. Soc.* **1942**, 570; (b) Ayrey, G.; Barnard, D.; Woodbridge, D. T. *J. Chem. Soc.* **1962**, 2089.
15. (a) Gould, E. S.; McCullough, J. D. *J. Am. Chem. Soc.* **1951**, *73*, 3196; (b) Rheinboldt, H.; Giesbrecht, E. *J. Am. Chem. Soc.* **1946**, *68*, 2671; (c) Lasser, R.; Weiss, R. *Chem. Ber.* **1913**, *46*, 2651.
16. Rheinboldt, H.; Giesbrecht, E. *J. Am. Chem. Soc.* **1947**, *69*, 2310.
17. (a) Surya prakash, G. K.; Hoole, D.; Ha, S. D.; Wilkinson, J.; Olah, A. G. *ARKIVOC* **2002**, *xiii*, 50; (b) Freeman, D. J.; Norris, R. K. *Aust. J. Chem.* **1976**, *29*, 2631; (c) Tenca, C.; Dossena, A.; Marchelli, R.; Casnati, G. *Synth. Commun.* **1981**, *11*, 141; (d) Auret, B. J.; Boyd, D. R.; Henbest, H. B.; Ross, S. *J. Chem. Soc. C* **1968**, 2372.
18. (a) Leicester, H. M.; Bergstrom, F. W. *J. Am. Chem. Soc.* **1931**, *53*, 4428; (b) Bhasin, K. K.; Gupta, V.; Bari, S. S.; Sharma, R. P. *Indian J. Chem.* **1991**, *30A*, 635; (c) Krief, A.; Dumont, W.; Gillin, F. *ARKIVOC* **2007**, *vii*, 51; (d) *Beilstein Handbuch Der Organischen Chemie*; Springer: Berlin, 1966; Vol. 6, p 346.
19. (a) Li, J.; Lue, P.; Zhou, X.-J. *Synthesis* **1992**, 281; (b) Bergman, J.; Engman, C. *Synthesis* **1980**, 569; (c) Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314.