Aqueous sodium hypochlorite mediated chemoselective oxidation of chalcogenides to monoxides and dioxides by microwave exposure

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Abstract: A solvent-free, rapid, and highly selective oxidation of sulfides, selenides, and tellurides (chalcogenides) to the corresponding monoxides (sulfoxides, selenoxides, and telluroxides) or the corresponding dioxides (sulfones, selenones, and tellurones) has been developed using aqueous sodium hypochlorite on solid supports by exposure to microwave. Chemoselectivity and quantitative yields have been attained in most cases.

Key words: chalcogenides, selective oxidation, sodium hypochlorite, microwave, solid support, solvent-free.

Résumé : On a mis au point une méthode rapide et n'impliquant aucun solvant pour l'oxydation hautement sélective des sulfures, de séléniures et des tellurures (chalcogénures) en monoxydes correspondants (sulfoxydes, sélénoxydes et telluroxydes) ou en dioxydes correspondants (sulfones, sélénones et tellurénones) à l'aide d'hypochlorite de sodium aqueux sur des supports solides exposés à des microondes. Dans la plupart des cas, on a atteint la chimiosélectivité accompagnée de rendements pratiquement quantitatifs.

Mots-clés : chalcogénures, oxydation sélective, hypochlorite de sodium, microonde, support solide, sans solvant.

[Traduit par la Rédaction]

Introduction

Oxidation of sulfur, selenium, and tellurium compounds has significant importance in organic chemistry, medicinal chemistry, and drug metabolism.[1] Sulfoxides, sulfones, organoselenium, and tellurium compounds are valuable synthons for carbon–carbon bond formation[2] as chiral auxiliaries[3] and for metal-centered catalysis.[4] The chemistry of selenium and tellurium oxides is of particular interest owing to their thermal instability[5] and their ability to stabilize adjacent anionic centers.[6] These transformations have been accomplished in a variety of ways.[7] Many of the reported methods suffer from poor yields, lack of generality, use of expensive reagents/catalysts, complex catalysts, toxic metallic compounds, or rare oxidizing reagents. On the other hand, selective oxidation of chalcogenides to their corresponding monoxides and dioxides with the same reagent system under adjusted reaction conditions is an important process, and only a few reports are available.[8] Diaryl and dialkyl telluroxides and tellurones are not well-explored compounds and have not received significant attention. Recently, microwave-enhanced chemical reactions on inorganic solid supports under solvent-free conditions[9] have attracted attention for various reasons. In view of the importance of these compounds, we decided to investigate the use of inexpensive aq. sodium hypochlorite for the selective oxidation of chalcogenides under microwave irradiation.

Experimental

All the products were known and were identified by comparison of the spectral and physical data with the literature.[7,8,10] Melting points were recorded on Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on PerkinElmer FTIR spectrum-2000. ^{1}H NMR spectra were recorded on FTNMR model R-600 Hitachi (60 MHz) with TMS as internal standard. The products were identified by co-TLC, melting point determination (mp), superimposable IR, and NMR spectra with authentic samples. Silica gel (100–200 mesh, for column chromatography) and neutral alumina (S.D. Fine) were used as inorganic solid supports. Sodium hypochlorite was used after estimation by the reported procedure.[11] Sulfides, selenides, and tellurides were prepared by the literature-reported methods.[12–17]

General procedure

General procedure for the oxidation of chalcogenides to dioxides

In a typical experiment, diphenyl sulfide (0.2 g, 1.074 mmol) was dissolved in dichloromethane (3 mL) and adsorbed over silica gel (100–200 mesh, 1.2 g). Aqueous sodium hypochlorite (0.65 mol/L, 3 mL) was added and mixed uniformly in a beaker. The reaction mixture was inserted in a silica bath (20 g of silica gel) and placed in a microwave oven (Model No.OM-9925-E, 800 W, 2450 MHz) and irradiated at 100 W

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Table 1. Oxidation of sulfides, selenides, and tellurides with aq. sodium hypochlorite to dioxides, supported on silica gel, under microwave exposure.

Entry	Substrate	Product	Time (min)	Yield (%)
1	Diphenyl sulfide	Diphenyl sulfone[8,10b,10c,10e]	10	93
2	Dibenzyl sulfide	Dibenzyl sulfone[8,10b,10e]	10	80
3	Di(*n*-dodecyl) sulfide	Di(*n*-dodecyl)sulfone[8,10b,10e]	9	82
4	Benzyl phenyl sulfide	Benzyl phenyl sulfone[8,10b,10e]	9	87
5	Phenyl *n*-propyl sulfide	Phenyl *n*-propyl sulfone[8,10b,10e]	10	82
6	*n*-Dodecyl phenyl sulfide	*n*-Dodecyl phenyl sulfone[8,10b,10e]	10	83
7	*p*-Chlorophenyl phenyl sulfide	*p*-Chlorophenyl phenyl sulfone[8,10b,10e]	10	84
8	*p*-Bromophenyl phenyl sulfide	*p*-Bromophenyl phenyl sulfone[8,10b,10e]	10	81
9	*m*-Chlorophenyl phenyl sulfide	*m*-Chlorophenyl phenyl sulfone[8,10b,10e]	10	80
10	Diphenyl selenide	Diphenyl selenone[7g,10b,10d,10e]	5	91
11	Dibenzyl selenide	Dibenzyl selenone[7g,10b,10d,10e]	6	88
12	Di(*p*-bromophenyl) selenide	Di(*p*-bromophenyl) selenone[7g,10b,10d,10e]	6	86
13	Di(*p*-methylphenyl) selenide	Di(*p*-methylphenyl) selenone[7g,10b,10d,10e]	6	86
14	Di(*p*-methoxyphenyl) selenide	Di(*p*-methoxyphenyl) selenone[7g,10b,10d,10e]	7	89
15	Di(*p*-methylphenyl) telluride	Di(*p*-methylphenyl) tellurone[7g,10b,10d,10e]	5	80
16	Di(*p*-methoxyphenyl) telluride	Di(*p*-methoxyphenyl) tellurone[7g,10b,10d,10e]	7	79
17	Di(*p*-bromophenyl) telluride	Di(*p*-bromophenyl) tellurone[7g,10b,10d,10e]	6	76
18	Methyl phenyl telluride	Methyl phenyl tellurone[7g,10b,10d,10e]	6	77

Note: Reactions were carried out using 3 mL of aq. NaOCl (0.65 mol/L) per mmol of substrate.

for 10 min. The progress of the reaction was monitored by TLC using petroleum ether as eluent, which showed complete disappearance of staring material after 10 min and formation of a new product having lower R_f (eluent: ethyl acetate), which was believed to be diphenyl sulphone by co-TLC. The reaction mixture was cooled to room temperature and the product was extracted with dichloromethane (2 × 5 mL). The combined dichloromethane extract was dried over anhyd. Na_2SO_4, filtered, and concentrated to afford 0.22 g (93%) of pure diphenyl sulfone as white solid identified by its mp 126 °C (lit.[10b] mp 128 °C), superimposable IR, and ^1H NMR spectra.

General procedure for the oxidation of chalcogenides to monoxides

In a typical experiment, diphenyl sulfide (0.2 g, 1.074 mmol) is dissolved in dichloromethane (3 mL) and adsorbed over neutral alumina (1.2 g). Aqueous sodium hypochlorite (1 mL, 0.65 mol/L) was added and mixed thoroughly in a beaker. The reaction mixture was inserted in an alumina bath (20 g of neutral alumina) and placed in a microwave oven (Model No.OM-9925-E, 800 W, 2450 MHz) and irradiated at 100 W for 3 min. After cooling for 1 min, another 1 mL of aq. sodium hypochlorite solution (0.65 mol/L) was added, and the mixture was stirred with a glass rod and irradiated again for 3 min. The progress of the reaction was monitored by TLC using petroleum ether as eluent. TLC showed complete disappearance of the starting material after 6 min and formation of a product having lower R_f (eluent: ethyl acetate), which was believed to be diphenyl sulfoxide by co-TLC. The reaction mixture was cooled to room temperature and the product was extracted with dichloromethane (2 × 5 mL). The combined dichloromethane extract was dried over anhyd. Na_2SO_4, filtered, and concentrated. The product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent. The white solid obtained was identified to be diphenyl sulfoxide (0.18 g, 82%) by mp 70 °C (lit.[10e] mp 71 °C), superimposable IR, and ^1H NMR spectra. Oxidation of selenides and tellurides was carried out in a similar fashion using 0.36 mol/L aq. NaOCl solution.

Results and discussion

We report herein an efficient, mild, and rapid method for the selective oxidation of chalcogenides (sulfides, selenides, and tellurides) to the corresponding monoxides (sulfoxides, selenoxides, and telluroxides) or the corresponding dioxides (sulfone, selenone, and tellurone) with inexpensive aq. sodium hypochlorite under microwave irradiation. Diphenyl sulfide was chosen as a model substrate for optimization. Oxidation of diphenyl sulfide was attempted with aq. NaOCl (0.65 mol/L) on different inorganic solid supports, e.g., neutral, acidic, and basic alumina; silica gel and montmorillonite K10 by adsorbing the substrate; and aq. sodium hypochlorite on solid support followed by exposing the reaction mixture to microwave irradiation (100 W). Oxidations on silica gel gave diphenyl sulfone in high yields (93%) in shorter time unlike other supports, which required longer reaction times and (or) gave reaction mixtures. Diphenyl selenide and di(*p*-methylphenyl) telluride also underwent oxidation to diphenyl selenone and di(*p*-methylphenyl) tellurone, respectively, under the same reaction conditions but required even shorter exposure to microwaves. Oxidation in the absence of solid support was incomplete, and a mixture of monoxide and dioxide was obtained. Subsequently, oxidation of various substituted aromatic and aliphatic sulfides, selenides, and tellurides was carried out with aq. sodium hypochlorite on silica gel solid support after exposure to microwaves to give the corresponding sulfones, selenones, and tellurones in high yields (eq. [1], Table 1).

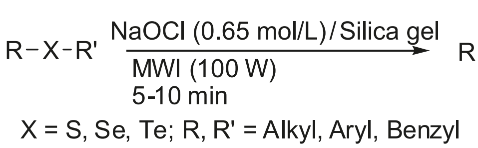
Table 2. Oxidation of sulfides, selenides, and tellurides with aq. sodium hypochlorite to monoxides under microwave exposure, supported on neutral alumina.

Entry	Substrate	Product	Time (min)^{a}	Yield (%)
1	Diphenyl sulfide	Diphenyl sulfoxide$^{8,10a–10c,10e}$	6 (3+3)	82
2	Di(*n*-butyl) sulfide	Di(*n*-butyl) sulfoxide^{8,10a,10b,10e}	5 (3+2)	87
3	Benzyl phenyl sulfide	Benzyl phenyl sulfoxide^{8,10a,10b,10e}	5 (3+2)	83
4	Phenyl *n*-propyl sulfide	Phenyl-*n*-propyl sulfoxide^{8,10a,10b,10e}	5 (3+2)	84
5	Di(*n*-dodecyl) sulfide	Di(*n*-dodecyl) sulfoxide^{8,10a,10b,10e}	6 (3+3)	81
6	Methyl phenyl sulfide	Methyl phenyl sulfoxide^{8,10a,10b,10e}	6 (3+3)	80
7	Dibenzyl sulfide	Dibenzyl sulfoxide^{8,10a,10b,10e}	6 (3+3)	91
8	*n*-Dodecyl phenyl sulfide	*n*-Dodecyl phenyl sulfoxide^{8,10a,10b,10e}	6 (3+3)	83
9	*n*-Butyl phenyl sulfide	*n*-Butyl phenyl sulfoxide^{8,10a,}	6 (3+3)	84
10	*p*-Chlorophenyl phenyl sulfide	*p*-Chlorophenyl phenyl sulfoxide^{10b,10e}	7 (3+4)	77
11	*p*-Bromophenyl phenyl sulfide	*p*-Bromophenyl phenyl sulfoxide^{10b,10e}	7 (3+4)	78
12	Diphenyl selenide	Diphenyl selenoxide^{10b,10e}	7 (3+4)	89
13	Di(*p*-methylphenyl) selenide	Di(*p*-methylphenyl) selenoxide^{10b,10e}	8 (4+4)	87
14	Di(*p*-chlorophenyl) selenide	Di(*p*-chlorophenyl) selenoxide^{10b,10e}	8 (4+4)	84
15	Di(*p*-methylphenyl) telluride	Di(*p*-methylphenyl) telluroxide^{10b,10e}	10 (5+5)	88
16	Di(*p*-methoxyphenyl) telluride	Di(*p*-methoxyphenyl) telluroxid^{10b,10e}	9 (5+4)	86
17	Di(*p*-bromophenyl) telluride	Di(*p*-bromophenyl) telluroxide^{10b,10e}	10 (5+5)	87

Note: Reactions were carried out using 2 mL of aq. NaOCl per mmol of substrate. Aqueous NaOCl solution (0.65 mol/L) was used for the oxidation of sulfides, and aq. NaOCl (0.36 mol/L) was used for the oxidation of selenides and tellurides.

^{a}Sodium hypochlorite used in two lots and the reaction mixture was irradiated in two intervals after a time gap of 1 min.

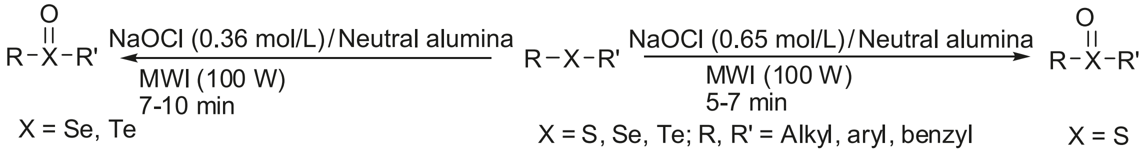
[1]



The applicability of the reagent under microwave irradiation was then investigated for the selective oxidation of different chalcogenides to their monoxides. During our exploratory experiments on diphenyl sulfide, we had observed that higher amount of diphenyl sulfoxide was formed when neutral alumina was used as the solid support. Subsequently, we have found that neutral alumina is the best solid support for selective oxidation to diphenyl sulfoxide using aq. sodium hypochlorite (0.65 mol/L) under microwave irradiation (100 W) only when sodium hypochlorite was added in two portions and the reaction mixture was irradiated twice with a 1 min time interval. No over oxidation to the sulfone was observed.

However, diphenyl selenide and di(*p*-methylphenyl) telluride gave mixtures of corresponding monoxides and dioxides under similar experimental conditions. Reaction conditions for the selective oxidation of selenides and tellurides were achieved with 0.36 mol/L aq. NaOCl solution. Diphenyl selenide and di(*p*-methylphenyl) telluride underwent selective oxidation with 0.36 mol/L aq. NaOCl solution under otherwise identical conditions. Thereafter, selective oxidation of a variety of sulfides was carried out with 0.65 mol/L aq. NaOCl solution, and oxidation of different selenides and tellurides was achieved with 0.36 mol/L aq. NaOCl solution supported on neutral alumina to give the corresponding monoxides in high yields in 5–10 min under microwave exposure (eq. [2], Table 2). The addition of sodium hypochlorite was done in two portions, and microwave exposure was done in two intervals with a gap of 1 min for the addition of reagent and cooling.

[2]



We conclude that chalcogenides can be selectively oxidized to their monoxides or dioxides in high yields by an environmentally benign and safe protocol using aq. sodium hypochlorite under microwave irradiation. Synergism of microwave methodology, use of aqueous reagent, and solvent-free conditions make this oxidation an attractive and facile synthetic protocol.

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