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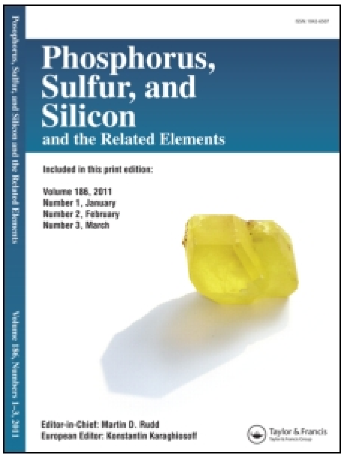

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Rapid Oxidation of Selenides, Selenoxides, Tellurides, and Telluroxides with Aqueous Sodium Hypochlorite

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RAPID OXIDATION OF SELENIDES, SELENOXIDES, TELLURIDES, AND TELLUROXIDES WITH AQUEOUS SODIUM HYPOCHLORITE

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A simple and convenient procedure for the rapid oxidation of a variety of selenides, selenoxides, tellurides, and telluroxides with aqueous sodium hypochlorite to selenones and tellurones, respectively, has been reported in dimethylformamide at ambient temperature.

Keywords: Aq. sodium hypochlorite; selenides; selenoxides; tellurides; telluroxides

The organic chemistry of the group **6a** elements selenium and tellurium has been actively investigated.[1] Many organo selenium and tellurium compounds are useful reagents or synthons in organic synthesis.[2] The chemistry of selenoxides and selenones is of particular interest owing to their synthetic usefulness, their thermal instability (fragmentation with olefin formation[3]), and their ability to stabilize adjacent anionic centers.[4] The chemistry of tellurium oxides is also important. Among these, the oxidizing potential of di(p-methoxyphenyl) telluroxide[5] and di(p-methyloxyphenyl) tellurone,[2b–c] toward some functional groups has been reported. As for synthesis, most of the earlier literature has reported two step synthesis of diaryl,[6] aryl alkyl,[7] and dialkyl selenones.[8] The methods are limited to some specific cases and many of them have been the subject of controversy.[7,9] Furthermore diaryl and dialkyl tellurone, the tellurium analogues of the well known sulphones, are not well defined compounds and have not received much attention. It is

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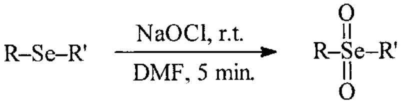
doubtful whether a compound corresponding to the formula R_2TeO_2 has ever been obtained in pure form.[2] In view of the importance of these compounds, we decided to investigate if inexpensive aq. sodium hypochlorite solution[10] could be used for the oxidation of selenides, selenoxides, tellurides, and telluroxides.

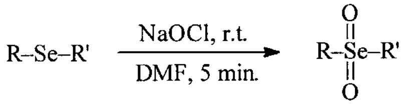
RESULTS AND DISCUSSION

This is the first report on the rapid oxidation of a variety of selenides (**1**) and selenoxides (**2**) to the corresponding selenones (**3**) and oxidation of tellurides (**4**) and telluroxides (**5**) to the corresponding telluroxides (**6**) in high yields with aq. sodium hypochlorite in dimethylformamide at ambient temperature to the corresponding tellurones in high yields at ambient temperature. First, oxidation of a variety of diaryl, dibenzyl, aryl alkyl, and dialkyl selenides (**1**) and selenoxides (**2**) was carried out. The oxidations are complete in ~5 min as monitored by thin layer chromatography using a 1:10 molar ratio of substrate to sodium hypochlorite (Eqs. 1 and 2). The reactions required careful quenching with minimum amount of acidified water to afford high yields of selenones (**3**). Quenching with an excess of acidified water and washing with excess water lowered the yields of the product. Thus oxidation of various substituted aromatic and aliphatic selenides (**1**), as well as selenoxides (**2**), was achieved successfully to afford the corresponding selenones (**3**) in high yields under the optimum reaction conditions. The optimum reaction conditions were found using diphenyl selenide and diphenyl selenoxide as model substrates. These results are listed in Table I. Oxidation of diphenyl selenide and dibenzyl selenide was not complete with aq. sodium hypochlorite in tetrahydrofuran, acetonitrile and dioxane even after prolonged reaction times and with high molar ratio of substrate to NaOCl. Therefore



$$\text{R–Se–R'} \xrightarrow[\text{DMF, 5 min.}]{\text{NaOCl, r.t.}} \text{R–}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{Se}}}\text{–R'} \qquad (1)$$

1a-k **3a-k**



$$\text{R–Se–R'} \xrightarrow[\text{DMF, 5 min.}]{\text{NaOCl, r.t.}} \text{R–}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{Se}}}\text{–R'} \qquad (2)$$

2a-h **3a-h**

TABLE I Oxidation of Selenide and Selenoxides with aq. Sodium Hypochlorite[a] in DMF at Ambient Temperature[b]

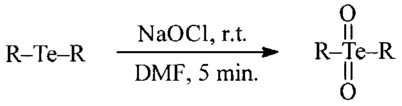
Substrate (**1**,**2**)	Selenone (**3**) % yield	Substrate	Selenone (**3**) % yield
1a Diphenyl selenide	79	**1k** p-methylphenyl-n-butyl selenide	85
1b Dibenzyl selenide	84	**2a** Diphenyl selenoxide	77
1c Di(p-methylphenyl) selenide	84	**2b** Dibenzyl selenoxide	69
1d Di(p-chlorophenyl) selenide	82	**2c** Di(p-methylphenyl) selenoxide	76
1e Di(p-bromophenyl) selenide	71	**2d** Di(p-chlorophenyl) slenoxide	84
1f Di(p-methoxyphenyl) selenide	83	**2e** Di(p-bromophenyl) selenoxide	83
1g Di(n-dodecyl) selenide	84	**2f** Di(p-methoxyphenyl) selenoxide	80
1h Di(n-propyl) selenide	81	**2g** Di(n-butyl) selenoxide	80
1i Di(n-butyl) selenide	82	**2h** Di(n-dodecyl) selenoxide	72
1j p-methylphenyl-n-propyl selenide	77		

[a] Reactions were carried out using 1:10 molar ratio of substrate to aq. NaOCl.

[b] Reactions were complete in 5 min as monitored by TLC.

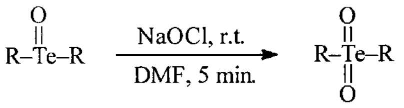
dimethylformamide is the solvent of choice for oxidation of selenides and selenoxides.

The applicability of the reagent was then extended to investigate the oxidation of different tellurides (**4**) and telluroxides (**5**) for which not many oxidizing agents are known. As a result, we report herein the rapid oxidation of various aromatic and aliphatic tellurides (**4**) and telluroxides (**5**) with aq. sodium hypochlorite in dimethylformamide at ambient temperature to the corresponding tellurones (**6**). The oxidation of tellurides and telluroxides were also complete in 5 min using a 1:10 molar ratio of substrate to NaOCl at ambient temperature (Eqs. 3 and 4). The tellurones (**6**) obtained in this process were pure and



$$R{-}Te{-}R \xrightarrow[\text{DMF, 5 min.}]{\text{NaOCl, r.t.}} R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}{-}R \qquad (3)$$

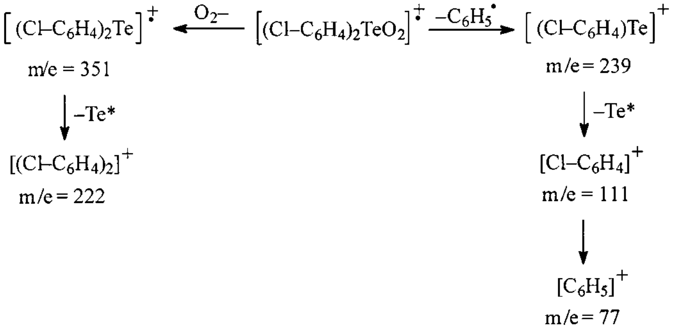
4a-e **6a-e**



$$R{-}\overset{\overset{O}{\|}}{Te}{-}R \xrightarrow[\text{DMF, 5 min.}]{\text{NaOCl, r.t.}} R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}{-}R \qquad (4)$$

5a-b **6a-b**

gave satisfactory spectroscopic data. Tellurones showed characteristic fragmentation pattern and is line with sulfur and selenium analogs. The fragmentation pattern is shown below (Scheme 1). Tellurides and telluroxides also did not undergo oxidation with aq. sodium hypochlorite in acletonitrile, tetrahydrofuran and dioxane. These results are summarized in Table II.



SCHEME 1

The oxidation of selenides and tellurides when carried out with a lower molar ratio of substrate to NaOCl showed the distinct formation of selenoxides and telluroxides, respectively, but the reactions were not complete even after prolonged reaction times. Attempts to carry out selective oxidation of selenides and tellurides to selenoxides and telluroxides, respectively, at low temperatures or under phase transfer conditions were unsuccessful due to competing rapid oxidation of selenoxides and telluroxides. We conclude that aq. sodium hypochlorite is a simple and convenient oxidising reagent for the

TABLE II Oxidation of Tellurides and Telluroxides with aq. Sodium Hypochlorite in DMF at Ambient Temperature

	Substrate (**4**,**5**)	Tellurone (**6**) % yield
4a	Di(p-methoxyphenyl) telluride	81
4b	Di(p-methylphenyl) telluride	78
4c	Di(p-chlorophenyl) telluride	78
4d	Di(p-bromophenyl) telluride	76
4e	Di(n-butyl) telluride	87
5a	Di(p-methylphenyl) telluroxide	68
5b	Di(p-chlorophenyl) telluroxide	85

rapid oxidation of a variety of selenides, selenoxides, tellurides and telluroxides.

EXPERIMENTAL

The melting points were determined on a Tropical Labequip apparatus and are uncorrected. IR were recorded on a Perkin Elmer FT-IR Spectrum 2000 and NMR spectra were recorded on Hitachi FT-NMR 60 MHz, respectively. Mass spectra were recorded on Jeol JMSD 300 spectrometer using electron impact method (70 eV).

Starting Materials

Dimethylformamide (E. Merck) was used in all the reactions after distillation. Sodium hypochlorite (S. D. Fine) was used in all the reactions after estimation[11] by the reported procedure. Aromatic selenides were prepared by slow addition of corresponding diazotized anilinium salt to potassium selenide solution in an ice bath.[12] Dibenzyl and aliphatic selenides were obtained from the reaction of corresponding halides with selenium and $NaBH_4$.[13] The reaction of elemental selenium with aryl magnesium halide and then with alkyl halides yielded the corresponding unsymmetrical selenides.[14] Tellurides were prepared by the treatment of sodium telluride with arenediazonium fluoroborates in DMF.[15] Synthesis of selenoxides involved two-step preparations (1) bromine addition to selenides to give selenide dibromide,[9] and (2) alkaline hydrolysis of selenide dibromide to give selenoxides.[6] Telluroxides were made by a similar route.[16]

General Procedure

In a typical reaction, in a 25 mL R.B. flask mounted over a magnetic stirrer and fitted with an air condenser, was placed diphenyl selenide (0.1 g, 0.4292 mmol) dissolved in 2 mL of DMF. 2.4 mL of aq. sodium hypochlorite (1.76 M, 4.292 mmol) was added by stirring. The reaction mixture was stirred magnetically at room temperature and progress of the reaction was monitored by tlc using petroleum ether as eluent. TLC of the reaction mixture showed complete disappearance of starting material after 5 min. A new product having lower R_f was formed as observed by tlc (eluent: ethyl acetate) and was believed to be diphenyl selenone by co-tlc. The reaction mixture was quenched after 15 min by dropwise addition of conc. HCl with stirring till a white precipitate appeared, this was followed by addition of water (5–7 mL). The solid was filtered at vacuum pump and dried under vacuum. The product was characterized by m.p. and spectral data. Reactions of other aromatic selenides and tellurides were carried out in similar manner. In case of aliphatic, unsymmetrical selenides, selenoxides and aliphatic tellurides, telluroxides, the reaction mixture was extracted with diethyl ether (2 × 15 mL) after acidification. The combined ethereal extract was dried over anhyd. $MgSO_4$ and concentrated on a rotary evaporator. The isolated products were identified by m.p. and spectral data.

6a: Di(p-methoxyphenyl) tellurone (white solid), m.p. $> 300°C$ (decompose) lit. m.p. $> 300°C$ (decompose);[2b] IR: 587, 699, 1065, 1177, 1253 (s), 1296, 1490 (s), 1583, 3431 (br) cm^{-1}; NMR ($CDCl_3$): δ 3.8 (s, 6H), δ 7.0–7.8 (br, 8H); m/e 375 (15), 342 (15), 267 (20), 148 (100), 104 (30), 77 (30).

6b: Di(p-methylphenyl) tellurone (white solid), m.p. 162–4°C; IR: 485 (s), 589 (s), 683 (s), 800 (s), 1063, 1185, 1392, 1490 (s), 1637, 3422.29 (br) cm^{-1}; NMR: δ 2.3 (s, 6H), δ 7.2–7.8 (br, 8H); mass m/e 310 (40), 220 (40), 181 (100), 166 (50), 77 (25).

6c: Di(p-chlorophenyl) tellurone (white solid), m.p. 285–7°C; IR : 488 (s), 591 (s), 685 (s), 728 (s), 813 (s), 1009 (s), 1089 (s), 1383, 1474 (s), 1567, 1656, 3371 (br) cm^{-1}; NMR: δ 7.0–7.6 (br, 8H); mass: m/e 351 (40), 240 (25), 221 (100), 111 (35), 77 (30).

6e: Di(n-butyl) tellurone (white solid), m.p. 177–80°C; IR: 543 (s), 654 (s), 890, 1090, 1463 (s), 1655, 3400 cm^{-1}; NMR: 1.1 (t, 6H), δ 3.0 (m, 8H), 3.6 (t, 4H); mass: m/e 242 (10), 185 (10), 57 (80), 41 (100).

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