# Indirect Electrolytic Oxidation of Thioamides Using Organotellurium as a Mediator

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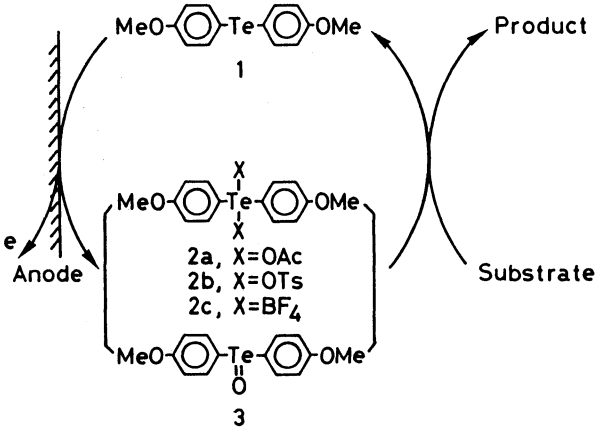
Bis(*p*-methoxyphenyl) telluride (**1**) electrochemically reacted with supporting electrolytes such as tetrabutylammonium acetate and tetraethylammonium tosylate under anhydrous conditions to give tellurium(IV) diacetate **2a** and ditosylate **2b**, respectively. On the other hand, **1** was electrolyzed in the presence of water to give telluroxide **3**. It has turned out that the tellurium compounds **2a** and **2b** like telluroxide **3** are mild oxidizing agents, but **2b** behaves differently in a reaction towards thioamide. Thus **2a** and **3** converted it into nitrile, while **2b** did it into 1,2,4-thiadiazole. An indirect electrolytic oxidation of thioamides with **1** as a mediator was examined under various conditions. As a result, nitriles or 1,2,4-thiadiazoles could be chemoselectively formed, depending on the intermediacy of **2a** or **3** as an active species for the former and **2b** for the latter.

There are few publications concerning the electrochemistry of organotellurium compounds. Recently Liftman and Albeck have reported that diaryl telluride electrochemically reacted with tetrabutylammonium perchlorate or lithium perchlorate as a supporting electrolyte under anhydrous conditions, giving diaryltellurium(IV) diperchlorate.[1] One might expect that the electrochemical oxidation of telluride in aqueous solution leads to the formation of telluroxide like the known conversion of sulfide into sulfoxide.[2] Diaryl telluroxide has been recently accepted as a versatile, mild oxidizing agent, which is reduced to the corresponding telluride in the oxidation reactions.[3,4] Taking into consideration that tellurium has the advantage of a lower oxidation potential than the other lighter chalcogens such as sulfur and selenium,[5] it looks promising to constitute a tellurium-mediated electrolytic oxidation. Such scope and limitation have been evaluated in this investigation. Here we like to report the electrochemical behavior of bis(*p*-methoxyphenyl) telluride (**1**) as well as an indirect electrolytic oxidation of thioamides using it as a mediator.

## Results and Discussion

The electrochemical behavior of telluride **1** in the presence of tetrabutylammonium acetate or tetraethylammonium tosylate as an electrolyte is shown in Table 1. The electrolysis in water-free acetonitrile gave tellurium(IV) compound **2a** or **2b** (Scheme 1). On the other hand, the electrolysis in the presence of water gave a mixture of **2** and telluroxide **3**. Tellurium(IV) compound **2** is considered to be formed via a mechanism of a one-electron oxidation followed by a dispropotionation or a second one-electron oxidative reaction of the radical intermediate **4** as shown in Scheme 2.[1] The formation of telluroxide **3** must take a similar pathway (Scheme 3). From additional experiments, **2** and **3** have turned out to be in an equilibrium state




Scheme 1.

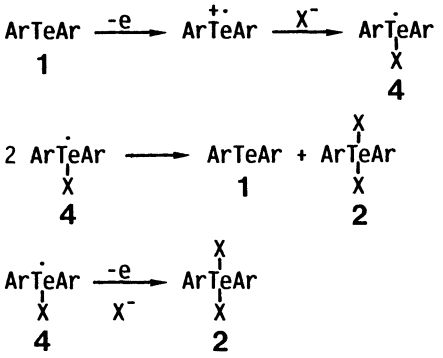
Table 1. Electrolysis of Bis(*p*-methoxyphenyl) Telluride (**1**) Leading to Tellurium(IV) Compound (**2**)[a] or Telluroxide (**3**)

| Run | Electrolyte | Solvent | Current density / mA cm$^{-2}$ | Electricity / F mol$^{-1}$ | Yield/% **2** | Yield/% **3** |
|---|---|---|---|---|---|---|
| 1 | $Bu_4NOAc$ | Anhyd MeCN | 8 | 2.2 | 95 | 0 |
| 2 | $Bu_4NOAc$ | 2% aq MeCN | 8 | 2.2 | 40 | 53 |
| 3 | $Bu_4NOAc$ | 10% aq MeCN | 8 | 2.2 | 42 | 56 |
| 4 | $Et_4NOTs$ | Anhyd MeCN | 8 | 2.4 | 93 | 0 |
| 5 | $Et_4NOTs$ | 2% aq MeCN | 8 | 2.4 | 85 | 7 |
| 6 | $Et_4NOTs$ | 10% aq MeCN | 8 | 2.3 | 39 | 58 |

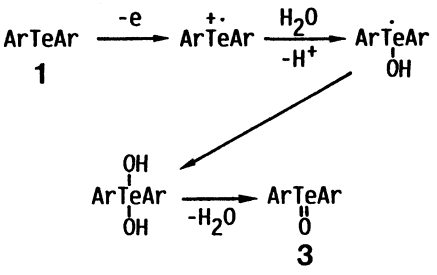
a) Bis(*p*-methoxyphenyl)tellurium diacetate (**2a**) for Runs 1—3 and ditosylate (**2b**) for Runs 4—6.

under electrolysis. These results suggest that it is possible to effect a chemoselective electrochemical reaction with **1** as a mediator, whose selectivity depends on the intermediacy of either **2** or **3** (Scheme 1).

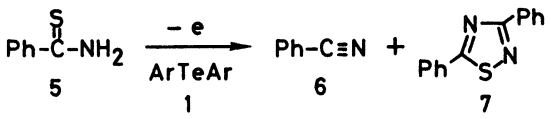
An indirect electrolytic oxidation with 5 mol% of telluride **1** as a mediator was examined for thiobenzamide (**5**) as a model substrate, since thioamide resists a direct electrochemical oxidation,[6] but is more reactive to telluroxide **3**. The electrolysis resulted in the formation of benzonitrile (**6**) and 3,5-diphenyl-1,2,4-thiadiazole (**7**) (Scheme 4). The selectivity evidently depended on the adopted electrolytic conditions as



Scheme 2.



Scheme 3.



Scheme 4.

Table 2. Indirect Electrolytic Oxidations of Thiobenzamide (**5**) to Benzonitrile (**6**) and 3,5-Diphenyl-1,2,4-thiadiazole (**7**) Using 5 mol% of Bis(*p*-methoxyphenyl) Telluride (**1**)

| Run | Electrolyte | Solvent | Current density | Electricity | Yield/% | |
|---|---|---|---|---|---|---|
| | | | mA cm$^{-2}$ | F mol$^{-1}$ | **6** | **7** |
| 1 | $Bu_4NOAc$ | Anhyd MeCN | 4 | 3.0 | 89 | Trace |
| 2 | $Bu_4NOAc$ | 2% aq MeCN | 4 | 2.7 | 95 | Trace |
| 3 | $Bu_4NOAc$ | 2% aq EtOH | 4 | 2.2 | 86 | Trace |
| 4 | $Bu_4NOAc$ | 2% aq EtOH | 3 | 2.1 | 90 | Trace |
| 5 | $Et_4NOTs$ | Anhyd MeCN | 4 | 3.6 | 5 | 90 |
| 6 | $Et_4NOTs$ | 0.5% aq MeCN | 8 | 2.4 | 72 | 11 |
| 7 | $Et_4NOTs$ | 10% aq MeCN | 4 | 2.7 | Trace | 92 |
| 8 | $Et_4NOTs$ | Anhyd EtOH | 4 | 2.4 | 0 | 95 |
| 9 | $Et_4NOTs$ | 0.5% aq EtOH | 4 | 3.6 | 0 | 90 |
| 10 | $Et_4NOTs$ | 2% aq EtOH | 4 | 2.7 | 0 | 98 |
| 11 | $Bu_4NBF_4$ | Anhyd MeCN | 8 | 3.0 | 0 | 72 |
| 12 | $Bu_4NBF_4$ | 0.5% aq MeCN | 8 | 2.4 | 44 | 32 |
| 13 | $Bu_4NBF_4$ | 1% aq MeCN | 8 | 2.4 | 70 | 11 |
| 14 | $Bu_4NBF_4$ | 2% aq MeCN | 8 | 2.4 | Trace | 74 |
| 15 | $Bu_4NBF_4$ | Anhyd EtOH | 4 | 2.4 | 0 | 79 |
| 16 | $Bu_4NBF_4$ | 2% aq EtOH | 4 | 2.4 | 0 | 82 |

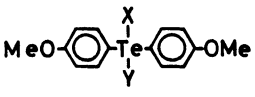
a) Determined by HPLC analysis.

Table 3. Reactions of Thiobenzamide (**5**) with Tellurium(IV) Compound (**2**) or Telluroxide (**3**) to Benzonitrile (**6**) and 3,5-Diphenyl-1,2,4-thiadiazole (**7**)[a]

| Run | Reagent | Solvent | Time | Yield/%[b] | | | Rate constant |
|---|---|---|---|---|---|---|---|
| | | | h | **5** | **6** | **7** | dm$^3$ mol$^{-1}$ h$^{-1}$ |
| 1 | **2a** | Anhyd MeCN | 12 | 0 | 80 | 18 | 151 |
| 2 | **2a** | 10% aq MeCN | 14 | 0 | 82 | 15 | 143 |
| 3 | **2b** | Anhyd MeCN | 16 | 0 | Trace | 90 | 137 |
| 4 | **2b** | 10% aq MeCN | 17 | 0 | Trace | 89 | 121 |
| 5 | **3** | Anhyd MeCN | 0.5 | 0 | 93 | Trace | 1913 |
| 6 | **3** | 2% aq MeCN | 1.5 | 0 | 91 | Trace | 876 |
| 7 | **3** | 10% aq MeCN | 20 | 11 | 81 | Trace | 50 |
| 8 | **3** | Anhyd EtOH | 24 | 60 | 31 | Trace | 4 |
| 9 | **3** | 2% aq EtOH | 23 | 49 | 43 | 5 | 5 |

a) Reaction temperature 25 °C. b) Determined by HPLC analysis.

summarized in Table 2. In order to elucidate these results, the reactivities of bis(*p*-methoxyphenyl)tellurium diacetate (**2a**), tellurium ditosylate (**2b**), and telluroxide (**3**) towards thiobenzamide (**5**) were investigated in detail. Thiobenzamide was treated with one molar equivalent reagent **2** or **3** under conditions specified in Table 3. The reaction was monitored by HPLC analysis and followed good second-order kinetics with 1:1 stoichiometry, a typical example being demonstrated in Fig. 1. As shown in Table 3, the reaction with telluroxide proceeded very fast in water-free acetonitrile, giving benzonitrile (**6**) in an excellent yield. However, the rate dropped drastically in acetonitrile containing some water or in ethanol with water or not. This less reactivity may be rationalized as due to the fact that telluroxide **3** with water or ethanol forms tellurium(IV) adducts **8a** or **8b**.[7] Both tellurium(IV) diacetate **2a** and ditosylate **2b** were also not so reactive as telluroxide **3**, but the reactivities were little affected by the presence of water and, as a result, surpassed that of telluroxide **3** in the presence of water. Furthermore, it should be noted that the reaction with **2a** gave rise to benzonitrile (**6**) and with **2b** to thiadiazole (**7**) as the main product.




**8a**, X=Y=OH
**8b**, X=OH, Y=OEt

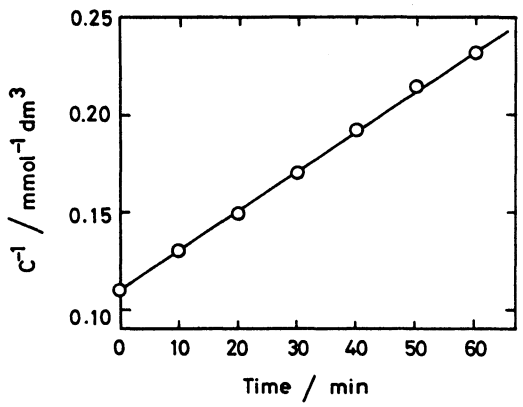
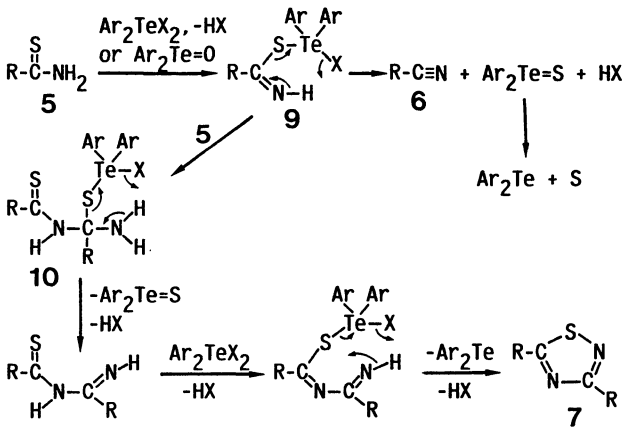



Fig. 1. Time dependence of the reciprocal of the concentration of **2b** in the equimolar reaction towards thiobenzamide in 10% aqueous acetonitrile at 25 °C.

As already indicated from Table 1, an active species in the electrolysis with tetrabutylammonium acetate as a supporting electrolyte is tellurium diacetate **2a** under water-free conditions and either **2a** or telluroxide **3** under water-containing conditions. Either species can give benzonitrile as the main product, being consistent with the indirect electrolyses of Table 2. On the other hand, the electrolysis with tetraethylammonium tosylate as electrolyte behaves differently. Tellurium ditosylate **2b** acted as an active species in anhydrous acetonitrile to give thiadiazole (**7**) in a high yield. The addition of a slight amount of water resulted in the formation of benzonitrile (**6**), indicating the intermediacy of telluroxide **3** as an active species. Further addition of water again gave thiadiazole (**7**). Telluroxide **3** with additional water can be understood to change to adduct **8a** which is less reactive than tellurium ditosylate **2b**. Such water dependence was not found in ethanol solution because the resulting telluroxide **3** with ethanol immediately forms a less reactive adduct **8b**. The electrolysis with tetrabutylammonium tetrafluoroborate as an electrolyte demonstrates a similar tendency. That is to say, tellurium bis(tetrafluo-




Scheme 5.

Table 4. Indirect Electrolytic Oxidations of Some Thioamides to Nitriles and 1,2,4-Thiadiazoles

| Run | Substrate | Method[a] | Isolated yield/% | |
|---|---|---|---|---|
| | | | Nitrile | Thiadiazole |
| 1 | *p*-Methoxythiobenzamide | A | 71 | 0 |
| 2 | *p*-Methoxythiobenzamide | B | 0 | 73 |
| 3 | *p*-Chlorothiobenzamide | A | 63 | 18 |
| 4 | *p*-Chlorothiobenzamide | B | 0 | 71 |
| 5 | *N,N'*-Diphenylthiourea | A | 80 | 6 |
| 6 | *N,N'*-Diphenylthiourea | B | 4 | 77 |

a) Method A: Current density 4mA cm$^{-2}$, Electricity 2.4 F mol$^{-1}$, Solvent 2% aq MeCN, Supporting electrolyte $Bu_4NOAc$. Method B: Current density 4 mA cm$^{-2}$, Electricity 2.4 F mol$^{-1}$, Solvent 2% aq EtOH, Supporting electrolyte $Et_4NOTs$.

roborate) **2c** is considered to be generated in the electrolysis and behaves like tellurium tosylate **2b** as an oxidizing agent, though it was not isolated.

Scheme 5 proposes a reasonable mechanism for the transformations of thioamide **5** into nitrile **6** and thiadiazole **7**.[4] A selection of both paths seems to depend on facility in eliminating an acid H-X in the initial common adduct **9**, in other words, basicity of the conjugated base X. Therefore, the elimination is favorable for X=OH and OAc, leading to nitrile **6**. On the other hand, it is hard for X=OTs and $BF_4$, so that the dimerization to **10** occurs, finally leading to thiadiazole **7**.

In conclusion, bis(*p*-methoxyphenyl) telluride (**1**) can be electrochemically oxidized to tellurium(IV) compound **2** or telluroxide **3**, enabling a chemoselective reaction using it as exemplified for the transformation of thiobenzamide to benzonitrile or diphenylthiadiazole. Table 4 demonstrates some other examples in which thioamides can be arbitarily transformed into either nitriles or thiadiazoles, depending on the two typical electrolytic conditions.

## Experimental

**Materials.** Bis(*p*-methoxyphenyl) telluride (**1**)[8] and telluroxide (**3**)[3] were prepared according to the literatures.

**Electrolytic Apparatus.** A 20 ml of H-type glass cell with a fine frit diving the anolyte and catholyte compartments was used for electrolyses. It was equipped with platinum plates (1 $cm^2$) as the working and counter electrodes. All electrolyses with carefully purified reagent, solvent, and supporting electrolyte were conducted at room temperature in a nitrogen atmosphere.

**General Procedure for Electrolyses of Bis(*p*-methoxyphenyl) Telluride (1).** A solution of dry acetonitrile (10 ml) containing tetrabutylammonium acetate (360 mg) was placed in the electrolytic cell. Bis(*p*-methoxyphenyl) telluride (**1**) (100 mg, 0.3 mmol) was added in the anolyte compartment and electrolyzed under a constant current density of 8 mA $cm^{-2}$. After 2.2 F (1 F=96485 C) $mol^{-1}$ of electricity had been passed, the mixture was thoroughly extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated in vacuo. Recrystallization of the residue from benzene gave colorless crystals of bis(*p*-methoxyphenyl)tellurium diacetate (**2a**); 131 mg (95%), mp 134.5—135.5 °C (lit,[9] mp 135—136 °C). $^1H$ NMR ($CDCl_3$) $\delta$=7.69 (d, $J$=9 Hz, 4H, ArH), 6.90 (d, $J$=9 Hz, 4H, ArH), 3.77 (s, 6H, OMe), and 1.93 (s, 6H, OCOMe); IR (KBr) 1630 (C=O), 1585, 1490 (Ar ring), 1290, 1255, and 1175 (C-O) $cm^{-1}$. Found: C, 47.02; H, 4.39%. Calcd for $C_{18}H_{20}O_6Te$ : C, 47.03; H, 4.39%.

When the electrolysis was carried out in aqueous acetonitrile, the isolated product was a mixture of **2a** and telluroxide **3** as shown in Table 1.

A similar electrolysis with tetraethylammonium tosylate electrolyte in dry acetonitrile deposited white crystals of bis(*p*-methoxyphenyl)tellurium ditosylate (**2b**) in the anolyte compartment, which was collected by filtration and washed with acetonitrile; 180 mg (93%), mp 257—260 °C. $^1H$ NMR ($CDCl_3$) $\delta$=7.67 (d, $J$=9 Hz, 4H, ArH), 7.37 (d, $J$=8 Hz, 4H, ArH), 6.96 (d, $J$=8 Hz, 4H, ArH), 6.80 (d, $J$=9 Hz, 4H, ArH), 3.72 (s, 6H, OMe), and 2.30 (s, 6H, Me); IR (KBr) 1585, 1495 (Ar ring), 1295, 1250, 1220, 1180, 1130, and 1015 ($SO_2O$ and C-O) $cm^{-1}$. Found: 49.09; H, 4.01%. Calcd for $C_{28}H_{28}O_8S_2Te$: C, 49.15; H, 4.12%.

**General Procedure for Indirect Electrooxidations of Thioamides to Nitriles or Thiadiazoles.** A mixture of thiobenzamide (**5**) (68.6 mg, 0.5 mmol) and bis(*p*-methoxyphenyl) telluride (**1**) (8.6 mg, 0.025 mmol) in 16 ml of dry acetonitrile containing tetrabutylammonium acetate (602 mg) was electrolyzed under a constant current density of 4 mA $cm^{-2}$. The reaction was monitored by HPLC (Microsorb C18 standard column, methanol eluent). After passage of 3.0 F $mol^{-1}$ of electricity (10 h), the starting material **5** was consumed, forming benzonitrile (**6**) (89%) and 3,5-diphenyl-1,2,4-thiadiazole (**7**) (trace). Both products **6** and **7** were isolated as colorless oil and as colorless crystals with mp 89.5—90.5 °C (lit,[10] mp 89—90 °C), respectively, from column chromatography of the concentrate of the reaction mixture on silica gel with 1 : 1 benzene-hexane eluent. All the products from the electrolyses shown in Table 4 were similarly isolated as colorless crystals and characterized: *p*-methoxybenzonitrile, mp 56—57 °C (lit,[11] mp 59.5—60.5 °C); *p*-chlorobenzonitrile, mp 94—94.5 °C (lit,[12] mp 92 °C); diphenylcyanamide, mp 73.5—74 °C (lit,[13] mp 73 °C); 3,5-bis(*p*-methoxyphenyl)-1,2,4-thiadiazole, mp 137—138 °C (lit,[10] mp 139—140 °C); 3,5-bis(*p*-chlorophenyl)-1,2,4-thiadiazole, mp 161.5—162 °C (lit,[10] mp 161—162 °C; 3,5-bis(diphenylamino)-1,2,4-thiadiazole, mp 154—154.5 °C (lit,[10] mp 155 °C).

**General Procedure for Reactions of Thiobenzamide (5) with Bis(*p*-methoxyphenyl)tellurium(IV) Compound 2 or Telluroxide 3.** A 15 ml solution of thiobenzamide (**5**) (18.7 mg) was treated with one molar equivalent reagent **2** or **3** under conditions specified in Table 3. The reaction was monitored by HPLC analysis (Microsorb C18 standard column, methanol eluent). The rate constant $k$ at 25 °C was evaluated by use of a second-order rate equation: $kt=(1/c)-(1/c_0)$ where $c$ is the time-dependent concentration of thiobenzamide and $c_0$ is the initial one. A plot of $1/c$ against time is linear with less than 7.4% standard deviation.

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telluride (**1**) showed an irreversible oxidation peak $E_p^{ox}$ at 0.80 V vs. Ag/AgCl while the corresponding sulfide at 1.35 V and selenide at 1.21 V (5 mol $m^{-3}$ acetonitrile solution, glassy carbon working electrode, 0.1 mol $dm^{-3}$ tetrabutylammonium perchlorate electrolyte, 100 mV $s^{-1}$ sweep rate).

6) Thiobenzamide (**5**) was sluggishly electrolyzed in a blank galvanostatic experiment, giving 3,5-diphenyl-1,2,4-thiadiazole (**7**) in ca. 20% yield.

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