JOC The Journal of Organic Chemistry

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Aerobic Oxidation of Thiols to Disulfides Catalyzed by Diaryl Tellurides under Photosensitized Conditions

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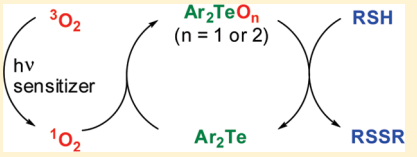
Supporting Information

ABSTRACT: Aerobic oxidation of thiols is efficiently catalyzed by diaryl tellurides such as bis(4-methoxyphenyl) telluride under photosensitized conditions to give the corresponding disulfides in good to excellent yields. In this catalytic system, the tellurone oligomer, produced by the reaction of a telluride with singlet oxygen, is assumed to be the active species and is capable of oxidizing 4 equiv of a thiol.



Oxidation of thiols to disulfides is an important process from both a synthetic and biological perspective.[1−6] A broad range of reagents and reaction conditions have been developed for the oxidative coupling of thiols. The most frequently employed oxidants include air, peroxides, heavy metal oxides and ions, halogens and halogenating agents, sulfoxides, nitro and azo compounds, and various combinations of these reagents.[2−4]

Considering recent trends focusing on the use of nonhazardous, green reagents, molecular oxygen has been regarded as an environmentally benign, sustainable oxidant. However, generally, the air oxidation of thiols is performed in the presence of a base or heavy metal ions.[7] Obviously, neutral and metal-free conditions are preferred. We previously reported that diorganotellurides efficiently catalyze the aerobic oxidation of phosphites to phosphates[8] and silanes to silanols[9] under photosensitized conditions. As an extension of our recent studies on the oxidation of organic substrates using organotellurium compounds,[8−11] we describe herein the diaryl telluride-catalyzed oxidation of thiols to disulfides using air as the terminal oxidant.

Organotellurium compounds have been previously used for the oxidation of thiols. For example, bis(4-methoxyphenyl) telluroxide (An_2TeO),[12,13] its polymer-bound derivative,[14] and aryltellurinic anhydrides[15,16] have been stoichiometrically used as mild and selective reagents for this oxidation. The catalytic use of diaryl tellurides for the oxidation of sulfur-containing compounds was reported by Ley and co-workers.[13,17] However, the reaction was limited to the conversion of thiocarbonyl compounds to their oxo analogues, and the catalytic cycle was initiated by bromination of the telluride, which was subsequently hydrolyzed under basic conditions. Recently, the catalytic activity of organotellurium compounds in H_2O_2 oxidation of thiols has been studied in connection with the development of glutathione peroxidase mimics.[18] Our study utilizes air oxidation to generate the active organotellurium oxidant, and to the best of our knowledge, represents the first report describing the aerobic oxidation of thiols to disulfides under photosensitized conditions.

Table 1 summarizes the results of an optimization study using various solvents and reagents with dodecanethiol as a model substrate. The optimum conditions are reported in entry 1 whereby a dichloromethane solution of the thiol (0.1 M), a catalytic amount of bis(4-methoxyphenyl) telluride (An_2Te, 1 mol %), and tetraphenylporphyrin (TPP, 0.1 mM), used as the photosensitizer, was stirred vigorously in an open flask and irradiated with a 500-W halogen lamp at 0 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy. The half-life time (T_{50}) of the starting thiol was determined to be 4 min and complete conversion was achieved by 15 min. Chromatographic purification of the reaction mixture gave didodecyl disulfide in 98% yield (entry 1).

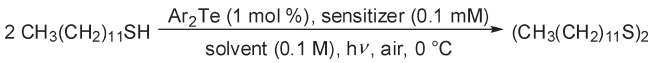
The oxidation reactions reported in Table 1 did not proceed in the dark or in the absence of the photosensitizer even after 4 h (data not shown). In the absence of the telluride catalyst, the oxidation gave a complex mixture due to possible overoxidation reactions, and the desired disulfide was obtained in only 12% yield after 4 h (51% conversion, entry 7). These results indicate that both telluride catalyst and singlet oxygen are essential for the clean transformation of the thiol to the disulfide.

The rate of this catalytic oxidation revealed a remarkable solvent dependence. Methanol and acetonitrile could not be used as a solvent owing to poor solubility of the substrate. Among the solvents tested (entries 1−3), dichloromethane gave the best results. We assume that the difference in the nature of active species generated in the different solvents may be responsible for the observed effect. However, the spectroscopic characterization of the active species was not possible because of its oligomeric structure (vide infra).

Other diaryl tellurides were also tested as catalysts. Diphenyl telluride (Ph_2Te) exhibited catalytic activity (T_{50} = 7.3 min, entry 4) comparable to that of An_2Te, whereas using bulky diaryl tellurides, such as Mes_2Te and Tip_2Te, significantly retarded the

Received: March 7, 2011
Published: April 11, 2011

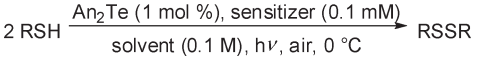
Table 1. Diaryl Telluride-Catalyzed Oxidation of Dodecanethiol to Didodecyl Disulfide



entry	Ar_2Te[a]	solvent (sensitizer[b])	T_{50} (min)[c,d]	time (min)	conversion (%)[d]	yield (%)[d]
1	An_2Te	CH_2Cl_2 (TPP)	4.0	15	>99	quant (98[e])
2	An_2Te	pyridine (HP)	10.4	30	>99	82[f]
3	An_2Te	benzene (TPP)	32.3	90	>99	quant
4	Ph_2Te	CH_2Cl_2 (TPP)	7.3	15	>99	quant
5	Mes_2Te	CH_2Cl_2 (TPP)	11.7	30	>99	86[f]
6	Tip_2Te	CH_2Cl_2 (TPP)	47.0	150	98	41[f]
7	none	CH_2Cl_2 (TPP)	–[g]	240	51	12[f]

[a] An = 4-methoxyphenyl, Mes = 2,4,6-trimethylphenyl, Tip = 2,4,6-triisopropylphenyl. [b] TPP = tetraphenylporphyrin, HP = hematoporphyrin. [c] Time required to reduce the thiol concentration by 50%. [d] Determined by ^{1}H NMR spectroscopy. [e] Isolated yield. [f] Accompanied by the formation of unidentified byproduct. [g] Not determined.

Table 2. An_2Te-Catalyzed Oxidation of Thiols to Disulfides



entry	RSH	solvent (sensitizer[a])	T_{50} (min)[b,c]	time (min)	RSSR (%)[d]
1	$PhCH_2SH$	CH_2Cl_2 (TPP)	3.8	15	quant
2	$HOCH_2CH_2SH$	CH_2Cl_2 (TPP)	4.4	15	90
3	$H_2NCH_2CH_2SH$	CH_2Cl_2 (TPP)	4.2	15	92
4	cyclohexanethiol	CH_2Cl_2 (TPP)	5.0	15	98
5	Me_3CSH	CH_2Cl_2 (TPP)	8.1	15	77
6	Ph_3CSH	CH_2Cl_2 (TPP)	12.2	30	99
7	PhSH	CH_2Cl_2 (TPP)	3.7	15	quant
8	$4\text{-}MeC_6H_4SH$	CH_2Cl_2 (TPP)	3.5	15	99
9	$4\text{-}MeOC_6H_4SH$	CH_2Cl_2 (TPP)	3.7	15	quant
10	$4\text{-}ClC_6H_4SH$	CH_2Cl_2 (TPP)	3.5	15	quant
11	$4\text{-}CF_3C_6H_4SH$	CH_2Cl_2 (TPP)	3.2	15	97
12	$4\text{-}MeSC_6H_4SH$	CH_2Cl_2 (TPP)	–[e]	15	85
13	$2,6\text{-}Cl_2C_6H_3SH$	CH_2Cl_2 (TPP)	4.5	15	88
14	2-mercaptopyridine	benzene (TPP)	–[e]	15	77
15	2-mercaptobenzothiazole	2-propanol–CH_2Cl_2 (TPP)	–[e]	30	90
16	*N*-acetylcysteine	2-propanol–CH_2Cl_2 (TPP)	6.0	15	quant
17	cysteine	2-propanol–H_2O (RB)	15.4	50	99
18	glutathione (GSH)	2-propanol–H_2O (RB)	25.9	60	quant

[a] TPP = tetraphenylporphyrin, RB = rose bengal. [b] Time required to reduce the concentration of thiol by 50%. [c] Determined by ^{1}H NMR spectroscopy. [d] Isolated yield. [e] Not determined because of overlapping ^{1}H NMR signals.

reaction rate (entries 5 and 6). In addition, the use of bulky tellurides induced the formation of some unidentified byproduct, probably due to overoxidation of the disulfide. For example, the yield of didodecyl disulfide in the Tip_2Te-catalyzed oxidation was only 41% after nearly complete conversion (98%) of the reaction (entry 6).

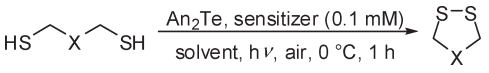
The present protocol was found to be advantageous for the oxidation of various thiols to the corresponding disulfides. Table 2 shows the yields of disulfides as well as the half-life times of the starting thiols. Aliphatic thiols were efficiently oxidized in good to excellent yields (entries 1–6). Furthermore, our protocol demonstrated selective oxidation of the thiol in the presence of hydroxy and amino functional groups (entries 2 and 3). As anticipated, the T_{50} values for secondary and tertiary thiols increased somewhat owing to steric constraints (entries 4–6).

For the oxidation of thiophenol and its substituted derivatives, the corresponding disulfides were obtained in good to excellent yields (entries 7–13) with no apparent substituent effects. Interestingly, the oxidation of 4-(methylthio)benzenethiol produced bis(4-(methylthio)phenyl) disulfide in 85% yield without affecting the methylthio group, which is known[19] to be oxidized by singlet oxygen (entry 12). We assume that the telluride catalyst is far more reactive than diorganosulfides toward singlet oxygen. In the case of sterically hindered 2,6-dichlorothiophenol, a slight increase in T_{50} was observed (entry 13).

Heterocyclic thiols, such as 2-mercaptopyridine and 2-mercaptobenzothiazole, can also be employed as substrates. Because these thiols are in equilibrium with their thioxo forms, the corresponding oxo compounds might be produced instead of the disulfides,

dx.doi.org/10.1021/jo200496r |*J. Org. Chem.* 2011, 76, 4173–4177

Table 3. Formation of Cyclic Disulfides



entry	X	An_2Te (mol %)	solvent (mM)	sensitizer[a]	yield (%)[b]
1	$-CH_2-$	1	benzene (10)	TPP	no reaction
2	$-CH_2CH_2-$	1	benzene (5)	TPP	69
3	$-CH_2CH_2CH_2-$	1	benzene (10)	TPP	45
4	$-CH(OH)CH(OH)-$	10	2-propanol-H_2O (10)	RB	75

[a] TPP = tetraphenylporphyrin, RB = rose bengal. [b] Isolated yield.

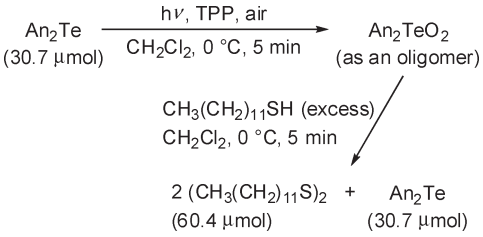
similar to the results reported by Ley and co-workers.[17] However, the oxidation of these thiols gave 2,2′-dipyridinyl and 2,2′-dibenzothiazolyl disulfides in 77% and 90% yields, respectively (entries 14 and 15), and we could not detect an isolable amount of the oxo products, 2(1*H*)-pyridinone and 2-benzothiazolinone.

Conversion of the biologically important cysteine, *N*-acetylcysteine, and glutathione into the corresponding disulfides was also investigated. Although the oxidation in protic solvents required a prolonged reaction time, clean and quantitative formation of cystine, *N*-acetylcystine, and the oxidized form of glutathione was observed (entries 16−18).

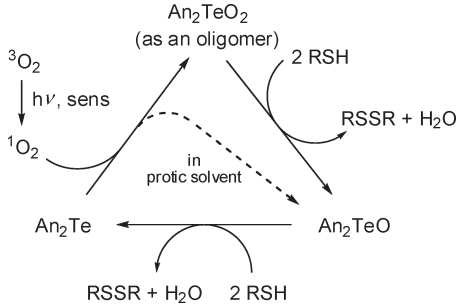
To investigate the formation of cyclic disulfides, we next examined the intramolecular cyclization of an α,ω-dithiol (Table 3). The oxidation of 1,4-butanedithiol with use of the established method resulted in formation of a complex mixture. The expected cyclization was best achieved when the reaction was performed in a diluted benzene solution (5 mM), giving 1,2-dithiane in 69% yield (entry 2). Similar treatment of 1,5-pentanedithiol afforded 1,2-dithiepane in 45% yield (entry 3), whereas the oxidation of 1,3-propanedithiol gave no reaction (entry 1). In the case of 1,4-dimercaptobutane-2,3-diol, a substrate known to readily oxidize to form the cyclic disulfide,[20] the yield of 1,2-dithiane-4,5-diol was moderate (75%), even though 10 mol % of the catalyst was used (entry 4). Although the cause remains unknown, the present oxidation method was not very effective for preparing cyclic disulfides. We assume that the intermolecular reaction of dithiols leading to oligomeric disulfides is faster than the intramolecular process.

To gain information about the active species in this catalytic system, the photosensitized oxidation of An_2Te was carried out in dichloromethane in the absence of the thiol substrate. ^1H and ^{13}C NMR analyses of the reaction mixture gave complex spectra that exhibited all the characteristics of an oligomeric mixture (see the Supporting Information). We hypothesize that the reaction of An_2Te with singlet oxygen affords An_2TeO_2, which exists as an oligomer like telluroxane, $(An_2TeO_2)_n$,[21] owing to the highly polarizable nature of the tellurium−oxygen bond. In fact, treatment of the oligomer, prepared from 30.7 μmol of An_2Te in dichloromethane, with an excess amount of dodecanethiol led to the immediate consumption of 4 equiv of the thiol to produce 60.4 μmol of didodecyl disulfide and the starting An_2Te, which was recovered quantitatively (Scheme 1). This suggests that each tellurium atom in the oligomer is associated with two reactive oxygen atoms, in support of our hypothesis. In contrast, similar treatment of An_2Te in 2-propanol gave An_2TeO as the sole product, consistent with our previous results obtained in an ethanol solution.[10,22] The resulting An_2TeO rapidly oxidized 2 equiv of dodecanethiol to give the corresponding disulfide in 98% yield along with a quantitative recovery of An_2Te.

Scheme 1. Formation of Tellurone Oligomer, $(An_2TeO_2)_n$, and Its Reaction with Dodecanethiol



Scheme 2. Plausible Catalytic Cycle for An_2Te-Catalyzed Oxidation of Thiols to Disulfides



On the basis of these findings, a catalytic cycle for the oxidation of thiols to disulfides is proposed as follows (Scheme 2). In aprotic solvents, the oligomeric An_2TeO_2 reacts with two thiols to give the disulfide and An_2TeO, which in turn oxidizes two more thiols to regenerate An_2Te. In protic solvents, however, An_2TeO is considered to be the only active species.

In conclusion, we have demonstrated that the air oxidation of various thiols was efficiently catalyzed by diaryl tellurides such as An_2Te under photosensitized conditions. Although spectroscopic characterization of the reactive intermediate generated in this catalytic cycle was not possible because of its oligomeric structure, the basic structural unit of the oligomer is assumed to be a diaryl tellurone that has two reactive oxygens, based on its capacity to oxidize 4 equiv of a thiol.

EXPERIMENTAL SECTION

General Procedure for Diorganotelluride-Catalyzed Oxidation of Thiols. A 0.1 M solution (10 mL) of thiol (1.00 mmol) and diaryl telluride (1 mol %) in the presence of an appropriate

dx.doi.org/10.1021/jo200496r |*J. Org. Chem.* 2011, 76, 4173–4177

photosensitizer (0.1 mM) was irradiated with a 500-W halogen lamp under aerobic conditions (in an open flask with vigorous stirring) for 1 h. An ice bath was used to maintain the reaction temperature around 0 °C during irradiation. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, and T_{50} of the starting thiol was determined by integration of the ^{1}H NMR signals with use of an appropriate internal standard. After the solvent was evaporated, the residue was analyzed by ^{1}H NMR spectroscopy to determine the final conversion. The disulfide product was isolated by using flash column chromatography on silica gel, and the yields are compiled in Tables 1, 2, and 3. Identification of the products was carried out by comparison of physical and spectral (^{1}H and ^{13}C NMR) data to those reported in the literature.

Didodecyl disulfide:[23] colorless solids, mp 30−31 °C (lit.[23] mp 29−31 °C); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7 Hz, 6H), 1.26 (m, 32H), 1.37 (quint, J = 7 Hz, 4H), 1.67 (quint, J = 7 Hz, 4H), 2.68 ppm (t, J = 7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.5, 29.2, 29.2, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 39.2 ppm.

Bis(phenylmethyl) disulfide:[23] colorless solids, mp 58−59 °C (lit.[23] mp 66−68 °C); ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 4H), 7.24−7.35 ppm (m, 10H); ^{13}C NMR ($CDCl_3$) δ 43.2, 127.4, 128.5, 129.3, 137.3 ppm.

Bis(2-hydroxyethyl) disulfide:[24] colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.05 (br s, 2H), 2.89 (t, J = 6 Hz, 4H), 3.92 ppm (br t, J = 6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 41.1, 60.3 ppm.

Bis(2-aminoethyl) disulfide:[25] colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.39 (br s, 4H), 2.76 (t, J = 6 Hz, 4H), 3.02 ppm (t, J = 6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 40.6, 42.5 ppm.

Dicyclohexyl disulfide:[23] colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.16−1.40 (m, 10H), 1.57−1.66 (m, 2H), 1.73−1.84 (m, 4H), 1.99−2.10 (m, 4H), 2.62−2.72 ppm (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.7, 26.1, 32.8, 50.0 ppm.

Di-*tert*-butyl disulfide:[26] colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.31 ppm (s, 18H); ^{13}C NMR ($CDCl_3$) δ 30.5, 46.1 ppm.

Bis(triphenylmethyl) disulfide:[27] colorless solids, mp 153−155 °C (lit.[27] mp 158−159 °C); ^{1}H NMR ($CDCl_3$) δ 7.23−7.37 ppm (m, 30H); ^{13}C NMR (acetone-d_6) δ 82.2, 127.8, 128.5, 129.0, 148.9 ppm.

Diphenyl disulfide:[23] colorless solids, mp 51−52 °C (lit.[23] mp 59−61 °C); ^{1}H NMR ($CDCl_3$) δ 7.22 (m, 2H), 7.30 (m, 4H), 7.50 ppm (m, 4H); ^{13}C NMR ($CDCl_3$) δ 127.1, 127.4, 129.0, 137.0 ppm.

Bis(4-methylphenyl) disulfide:[7d] colorless solids, mp 53−54 °C (lit.[7d] mp 51−53 °C); ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 6H), 7.11 (d, J = 8 Hz, 4H), 7.39 ppm (d, J = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 21.1, 128.5, 129.8, 133.9, 137.4 ppm.

Bis(4-methoxyphenyl) disulfide:[7b] colorless solids, mp 34−35 °C (lit.[7b] mp 41−43 °C); ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 6H), 6.84 (d, J = 9 Hz, 4H), 7.40 ppm (d, J = 9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.6, 128.4, 132.6, 159.9 ppm.

Bis(4-chlorophenyl) disulfide:[28] colorless solids, mp 65−66 °C (lit.[28] mp 71−72 °C); ^{1}H NMR ($CDCl_3$) δ 7.28 (d, J = 9 Hz, 4H), 7.40 ppm (d, J = 9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 129.3 (overlapped), 133.6, 135.1 ppm.

Bis(4-(trifluoromethyl)phenyl) disulfide:[29] colorless oil; ^{1}H NMR (DMSO-d_6) δ 7.64 (d, J = 9 Hz, 4H), 7.65 ppm (d, J = 9 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ 124.1 (q, J = 272 Hz), 126.4, 126.8, 128.1 (q, J = 32 Hz), 140.7 ppm.

Bis(4-(methylthio)phenyl) disulfide:[30] colorless solids, mp 80−82 °C (lit.[30] mp 90 °C); ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 6H), 7.17 (d, J = 9 Hz, 4H), 7.39 ppm (d, J = 9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 15.7, 126.9, 129.4, 133.4, 138.5 ppm.

Bis(2,6-dichlorophenyl) disulfide:[7f] colorless solids, mp 78−82 °C (lit.[7f] mp 80−83 °C); ^{1}H NMR ($CDCl_3$) δ 7.20 (dd, J = 9 and 7 Hz, 2H), 7.34 (d, J = 9 Hz, 2H), 7.34 ppm (d, J = 7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 128.5, 131.1, 134.2, 141.4 ppm.

Bis(2-pyridinyl) disulfide:[31] colorless solids, mp 53−54 °C (lit.[31] mp 55−56 °C); ^{1}H NMR ($CDCl_3$) δ 7.11 (m, 2H), 7.59−7.65 (m, 4H), 8.47 ppm (m, 2H); ^{13}C NMR ($CDCl_3$) δ 119.6, 121.1, 137.3, 149.5, 158.9 ppm.

Bis(2-benzothiazolyl) disulfide:[7f] colorless solids, mp 178−179 °C (lit.[7f] mp 177−179 °C); ^{1}H NMR ($CDCl_3$) δ 7.36 (ddd, J = 8, 7, and 1 Hz, 2H), 7.47 (ddd, J = 8, 7, and 1 Hz, 2H), 7.77 (d, J = 8 Hz, 2H), 7.94 ppm (d, J = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 121.3, 122.7, 125.3, 126.6, 136.1, 154.5, 167.9 ppm.

***N,N′*-Diacetyl-L-cystine:**[32,33] amorphous solids; $[\alpha]^{24}_D$ −102.95 (c 1.06, D_2O) [lit.[33] $[\alpha]^{24}_D$ −106.51 (c 1.12, D_2O)]; ^{1}H NMR (D_2O) δ 2.04 (s, 6H), 3.02 (dd, J = 14 and 9 Hz, 2H), 3.15 (dd, J = 14 and 4 Hz, 2H), 4.71 ppm (dd, J = 9 and 4 Hz, 2H); ^{13}C NMR (D_2O) δ 22.1, 39.0, 52.2, 174.2, 174.6 ppm.

L-Cystine:[34,35] colorless solids, mp 226−227 °C dec (lit.[35] mp 240−242 °C dec); $[\alpha]^{20}_D$ −195.32 (c 1.00, 1 M HCl) [lit.[35] $[\alpha]^{20}_D$ −205.17 (c 1.02, 1 M HCl)]; ^{1}H NMR (4% NaOD in D_2O) δ 2.85 (dd, J = 14 and 8 Hz, 2H), 3.06 (dd, J = 14 and 5 Hz, 2H), 3.52 ppm (dd, J = 8 and 5 Hz, 2H); ^{13}C NMR (4% NaOD in D_2O) δ 44.0, 55.3, 181.1 ppm.

Glutathione disulfide:[28,36] colorless solids, mp 170−172 °C (lit.[28] mp 178−180 °C); $[\alpha]^{20}_D$ −195.32 (c 1.00, 1 M HCl), $[\alpha]^{24}_D$ −96.57 (c 2.03, H_2O) [lit.[36] $[\alpha]^{20}_D$ −108 (c 2, H_2O)]; ^{1}H NMR (D_2O) δ 2.13 (dd, J = 7 and 7 Hz, 2H), 2.14 (dd, J = 7 and 7 Hz, 2H), 2.49 (ddd, J = 15, 7, and 6 Hz, 2H), 2.53 (ddd, J = 15, 7, and 6 Hz, 2H), 2.94 (dd, J = 14 and 9 Hz, 2H), 3.24 (dd, J = 14 and 5 Hz, 2H), 3.80 (dd, J = 6 and 6 Hz, 2H), 3.94 (s, 4H), 4.71 ppm (dd, J = 9 and 5 Hz, 2H); ^{13}C NMR (D_2O) δ 26.5, 31.7, 39.1, 42.0, 53.0, 54.1, 172.9, 173.9, 175.2 ppm.

1,2-Dithiane:[37] colorless solids, mp 26−27 °C (lit.[37] mp 33−34 °C); ^{1}H NMR ($CDCl_3$) δ 1.97 (br s, 4H), 2.84 ppm (br s, 4H); ^{13}C NMR ($CDCl_3$) δ 27.8, 33.3 ppm.

1,2-Dithiepane:[38]**.** colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.74−1.80 (m, 2H), 1.99−2.06 (m, 4H), 2.83 ppm (t, 4H); ^{13}C NMR ($CDCl_3$) δ 26.2, 30.2, 39.4 ppm.

***trans*-1,2-Dithiane-4,5-diol:**[39] colorless solids, mp 128−130 °C (lit.[39] mp 128−130 °C); ^{1}H NMR (CD_3OD) δ 2.82−2.92 (m, 2H), 3.00−3.08 (m, 2H), 3.46−3.53 ppm (m, 2H); ^{13}C NMR (CD_3OD) δ 41.7, 75.5 ppm.

Formation of Tellurone Oligomer and Its Reaction with Dodecanethiol (Scheme 1). A CH_2Cl_2 solution (30 mL) of An_2Te (10.3 mg, 30.7 μmol) in the presence of TPP (0.1 mM) was irradiated with a 500-W halogen lamp under aerobic conditions at 0 °C for 5 min. After the solvent was evaporated, the residue was analyzed by ^{1}H and ^{13}C NMR spectroscopy and then dissolved in CH_2Cl_2 (3 mL). To this solution was added an excess amount of dodecanethiol (47.3 mg, 234 μmol) and the solution was stirred at 0 °C for 5 min. The reaction mixture was directly analyzed by ^{1}H NMR spectroscopy, and the amounts of didodecyl disulfide (60.4 μmol) and An_2Te (30.7 μmol) were determined by integration of the ^{1}H NMR signals.

■ ASSOCIATED CONTENT

Supporting Information. General information and copies of ^{1}H and ^{13}C NMR for disulfides and $(An_2TeO_2)_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

M.O. would like to acknowledge Tokai University for financial support.

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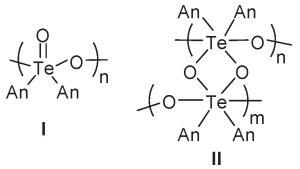

I

II

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