Dendrimeric Organotelluride Catalysts for the Activation of Hydrogen Peroxide. Improved Catalytic Activity through Statistical and Stereoelectronic Effects

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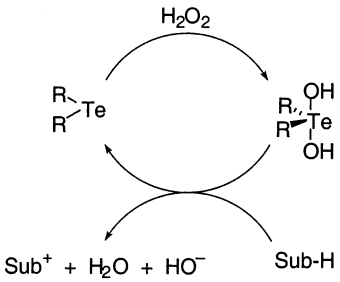
Dendrimeric polyorganotellurides are prepared in high yield using propyloxy spacers to connect the organotelluride groups to the core molecules. The polyorganotellurides catalyze the oxidation of thiophenol with hydrogen peroxide to give diphenyl disulfide in homogeneous solutions (5% CH_2Cl_2/MeOH or 46% CH_2Cl_2/MeOH). The polyorganotellurides with two, three, four, and six catalytic groups show roughly statistical increases for the number of catalytic groups relative to the corresponding monotellurides. Catalysts containing [4-(dimethylamino)-phenyl]telluro groups and *n*-hexyltelluro groups are oxidized more rapidly by hydrogen peroxide and also show greater catalytic activity than the corresponding catalysts containing phenyltelluro groups. A combination of statistical effects and stereoelectronic effects give a 26-fold increase in catalytic activity from 1-phenoxy-3-(phenyltelluro)propane (**23a**; $\nu_0 = 12$ μM min^{-1}) to dendrimer **22c** with six *n*-hexyltelluro groups ($\nu_0 = 312$ μM min^{-1}) for the oxidation of 1.0×10^{-3} M PhSH with 3.75×10^{-3} M H_2O_2 in the presence of 1.0×10^{-5} M catalyst. The rate of appearance of PhSSPh, with a molar extinction coefficient, ϵ, of 1.24×10^{-3} L mol^{-1} cm^{-1} at 305 nm, was monitored at 305 nm.

While H_2O_2 is a powerful oxidant thermodynamically, many of the reactions of H_2O_2 are limited by the kinetics of reaction, as illustrated by the oxidation of halides to the corresponding halogen/hypohalous acid[1] and the oxidation of thiols to disulfides.[2] Nature has developed a variety of peroxidase enzymes to accelerate these reactions of H_2O_2 and other peroxy compounds, and chemists have designed synthetic catalysts to mimic the peroxidase enzymes.[3] Among these latter catalysts, diorganotellurides have been excellent catalysts for the activation of H_2O_2 in these particular reactions.[2,4]

The diorganotellurides undergo two-electron redox processes at the Te atom during the catalytic cycle, as shown in Scheme 1.[2,4,5] Peroxide oxidation of the diorganotelluride gives the corresponding oxide (or its hydrate), which then acts as an oxidant (kinetically superior to H_2O_2) for a variety of substrates (Sub-H). The diorganotelluride is regenerated in the process to resume the catalytic cycle. The rate-limiting step in the catalytic process is the rate of oxidation of the diorganotelluride.[4a,5b]

Scheme 1



For the diorganotellurides, catalytic activity with H_2O_2 will be a balance between the rate of oxidation of the Te atom with H_2O_2 and the rate of reductive elimination to form product and to regenerate catalyst. Traditionally, the molar activity of catalysts has been optimized through structure−activity relationships derived from substituent changes. However, stereoelectronic effects can only go so far with respect to increasing rates of oxidation of the Te atom. We have shown enhanced catalytic activity in dendrimeric[6] diorganotelluride catalysts[7] in which statistical increases in catalytic activity in two-phase systems were noted by

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Scheme 2

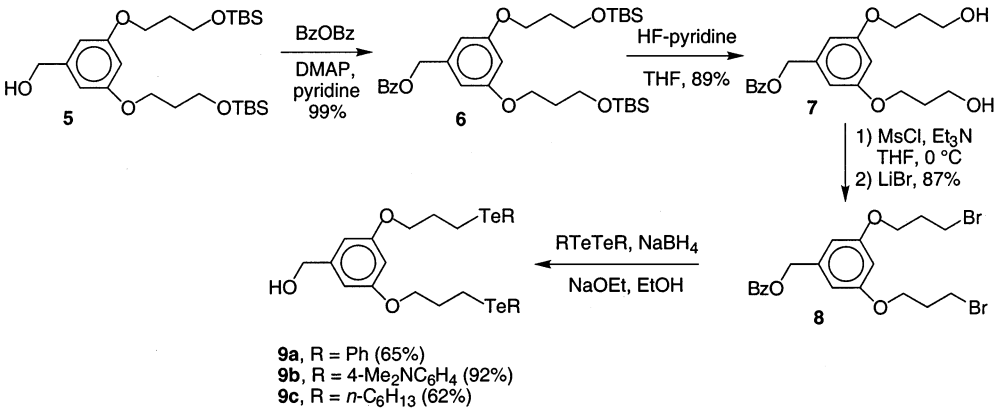
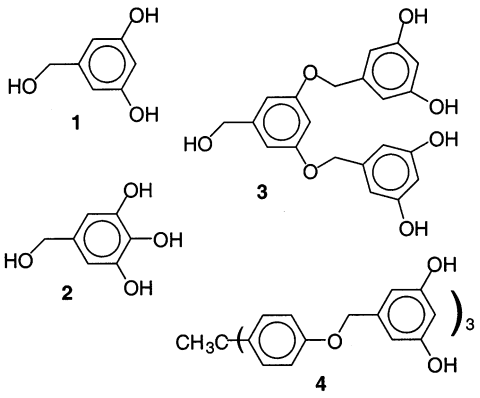


Chart 1



incorporating the catalytic telluride functionality at the end of each dendrimer arm. Herein, we describe the thiol peroxidase like activity of dendrimeric organotellurides in a homogeneous system[8] and examine not only statistical effects but also stereoelectronic effects in the telluride substituents.

Results and Discussion

Synthesis of Catalysts. The dendrimer architecture supporting the catalytic organotelluride groups must be stable to H_2O_2. We have demonstrated that Fréchet-type dendrimers (Chart 1) based on 3,5-dihydroxybenzyl alcohol (**1**)[9] and 3,4,5-trihydroxybenzyl alcohol (**2**)[10] are well-suited to this task.[7] Compounds **1** and **2** provide two and three points of attachment, respectively, through the phenolic groups, leaving the benzyl alcohol functionality for further functionalization. Linking three molecules of **1** together gives four points of attachment in dendritic wedge **3** through the phenolic groups, while linking three molecules of **1** to 1,1,1-tris(4-hydroxyphenyl)ethane gives the first-generation dendrimer **4**, with six points of attachment.[9]

The synthesis of organotelluride catalysts based on 3,5-dihydroxybenzyl alcohol (**1**) is shown in Scheme 2. 3,5-Bis[3-((*tert*-butyldimethylsilyl)oxy)propyl-1-oxy]benzyl alcohol (**5**)[7] was converted to the corresponding benzoate **6** in 99% isolated yield with benzoic anhydride and pyridine in the presence of catalytic DMAP. The silyl protecting groups were removed with HF−pyridine to give diol **7** in 89% isolated yield. Diol **7** was converted to the corresponding dibromide **8** in two steps.[11] The mesylate was first prepared, but not isolated, and was then treated in situ with lithium bromide to give dibromide **8** in 87% isolated yield. The addition of PhTeNa to **8** gave **9a** with two phenyltelluro groups in 65% isolated yield, 4-$Me_2NC_6H_4$TeNa (**9b**) with two [(dimethylamino)phenyl]telluro groups in 92% isolated yield, and *n*-C_6H_{13}TeNa (**9c**) with two hexyltelluro groups in 62% isolated yield.

The structures of tellurides **9** followed directly from mass spectrometry and the symmetry of both ^{1}H and ^{13}C NMR spectra. The electrospray mass spectra of all three tellurides **9** displayed the characteristic isotope clusters for molecules with two Te atoms (illustrated for **9a** in Figure S1, in the Supporting Information).

The synthesis of organotelluride catalysts based on 3,4,5-trihydroxybenzyl alcohol (**2**) is shown in Scheme 3. Methyl gallate was treated with excess 3-[(*tert*-butyldimethylsilyl)oxy]-1-bromopropane in the presence of K_2CO_3 to give ester **10** in 50% isolated yield, which was then reduced to benzyl alcohol **11** in 87% isolated yield with $LiAlH_4$. Compound **11** was converted to the benzoate ester **12** in 99% isolated yield as described, which was then desilylated with HF−pyridine to give triol **13** in 92% isolated yield. As before, the hydroxyl groups were converted via the mesylate to the corresponding bromides[11] to give **14** in 62% overall yield. The addition of excess PhTeNa to **14** gave tritelluride **15a** in 56% isolated yield, that of 4-$Me_2NC_6H_4$TeNa gave tritelluride **15b** in 94% isolated yield, and that of *n*-C_6H_{13}TeNa gave tritelluride **15c** in 56% isolated yield.

The structures for tritellurides **15** directly followed from mass spectrometry as well as the symmetry of their ^{1}H and ^{13}C NMR spectra. The NMR spectra of compounds **15** displayed the same C_2 symmetry as those of compounds **9** but displayed the extra signals from the additional 4-[((organotelluro)propyl)oxy] group. The electrospray mass spectra of compounds **15** displayed the characteristic isotope clusters for three Te atoms (il-

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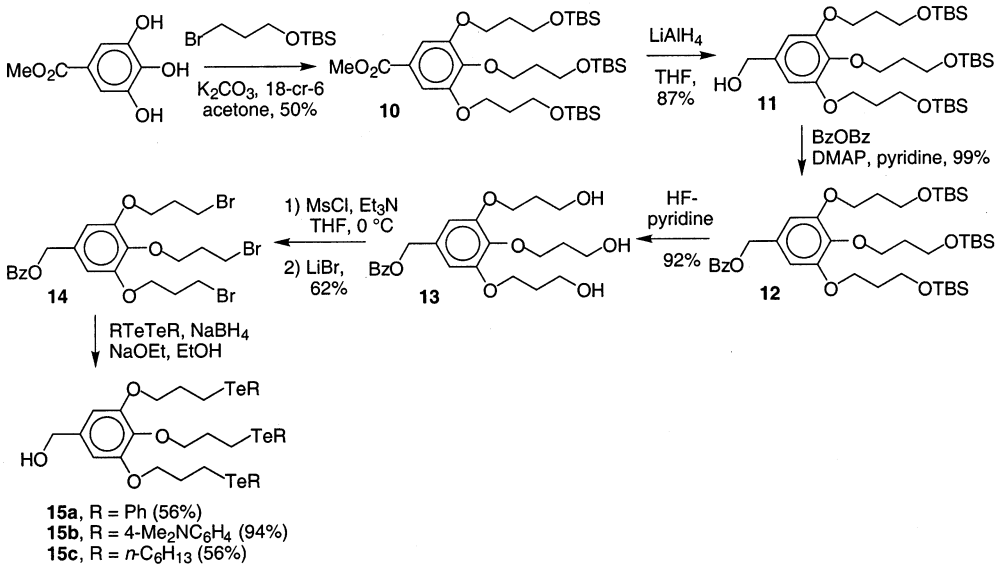
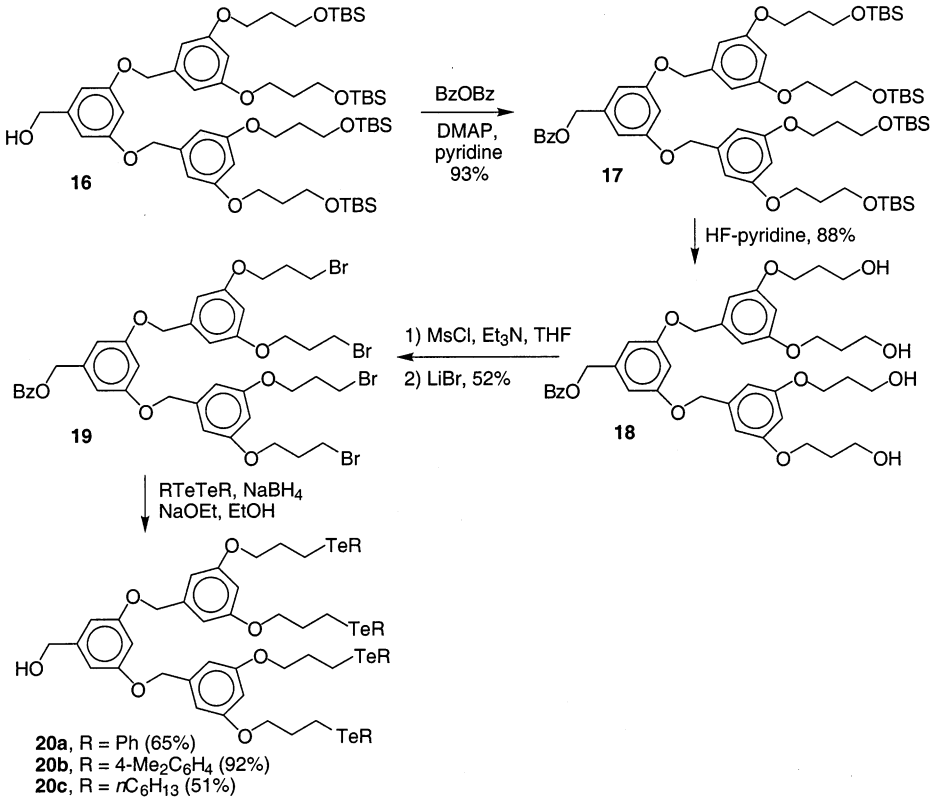
Scheme 3



15a, R = Ph (56%)
15b, R = 4-$Me_2NC_6H_4$ (94%)
15c, R = *n*-C_6H_{13} (56%)

Scheme 4



20a, R = Ph (65%)
20b, R = 4-$Me_2C_6H_4$ (92%)
20c, R = *n*C_6H_{13} (51%)

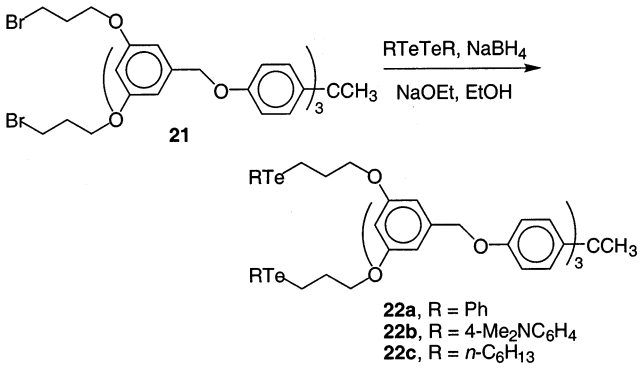
lustrated for **15c** in Figure S2, in the Supporting Information).

The synthesis of tetratelluride catalysts based on the dendritic wedge **3** is shown in Scheme 4. Benzyl alcohol **16**[7] was converted to the benzoate **17** in 93% isolated yield with benzoic anhydride, as previously described. The four silyl groups were removed with HF−pyridine to give tetraol **18** in 88% isolated yield. As before, the hydroxyl groups were converted via the mesylate to the corresponding bromides[11] to give tetrabromide **19** in 52% overall yield. The addition of excess PhTeNa to **19** gave tetratelluride **20a** in 65% isolated yield, that of 4-$Me_2NC_6H_4$TeNa gave tetratelluride **20b** in 92% isolated yield, and that of *n*-C_6H_{13}TeNa gave tetratelluride **20c** in 51% isolated yield.

The structures of tetratellurides **20** followed directly from the ^{1}H and ^{13}C NMR spectra as well as the electrospray mass spectra. The ^{13}C NMR spectra of **20a**−**c** displayed the expected 17, 18, and 19 lines, respectively, for the tetratelluride. The mass spectra of compounds **20** displayed the characteristic isotope clusters for molecules containing four Te atoms (illustrated for **20a** in Figure S3, in the Supporting Information).

The synthesis of hexatelluride catalysts based on the first-generation dendrimer **4** is shown in Scheme 5. Hexabromide **21**[7] was treated with excess PhTeNa to

Scheme 5



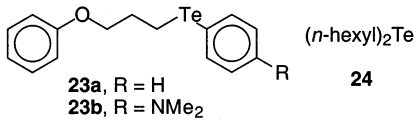
give hexatelluride **22a**[7] in 82% isolated yield, with excess 4-$Me_2NC_6H_4TeNa$ to give hexatelluride **22b** in 82% isolated yield, and with excess *n*-$C_6H_{13}TeNa$ to give hexatelluride **22c** in 45% isolated yield.

Unlike tellurides **9**, **15**, and **20**, the hexatellurides **22** did not give a parent ion by mass spectrometry under several soft ionization conditions (FAB, electrospray ionization). The ^1H and ^{13}C NMR spectra of compounds **22** were consistent with the proposed structures. Dendrimer **22a**, terminating in 6 phenyltelluro groups, displayed the expected 18 ^{13}C NMR signals for the first-generation dendrimer. Similarly, dendrimer **22b**, terminating in 6 [4-(dimethylamino)phenyl]telluro groups, displayed the expected 19 signals from the additional aliphatic signal of the dimethylamino substituent. Dendrimer **22c**, terminating in 6 hexyltelluro groups, displayed the expected 20 signals, including the additional 6 aliphatic carbon signals. The roughly 25−30 ppm upfield shift observed in the ^{13}C chemical shift for the aliphatic C's bonded to Te in compounds **22** relative to Br in hexabromide **21** (δ 32.3)[7] was diagnostic for the displacement of bromides by the organotelluride groups. For **22a**, this signal is observed at δ 4.3. For **22b**, this signal is observed at δ 4.1. For **22c**, terminating in hexyltelluro groups, two highly shielded aliphatic carbons are observed at δ 3.1 and −2.0, which is consistent with a dialkyl telluride.

Oxidation of Telluride Catalysts with Hydrogen Peroxide. For the catalytic cycle shown in Scheme 1, the rate-determining step in all systems examined to date is the rate of oxidation of the telluride,[4a,5b] which is accelerated by electron-donating substituents. In contrast, reductive elimination of the oxidized substrate is accelerated by electron-withdrawing substituents.[4b,12] The 4-(dimethylamino)phenyl and *n*-hexyl substituents are both more electron-donating than the phenyl substituent, which suggests that organotelluride catalysts bearing the former substituents should be more readily oxidized than the phenyl series of catalysts. The monotellurides **23** and di-*n*-hexyltelluride (**24**)[13] shown in Chart 2 are model catalytic systems for the dendrimeric organotelluride catalysts **9**, **15**, **20**, and **22**, and the rates of oxidation of the monotellurides should predict the relative rates of oxidation in the dendrimeric catalysts.

1-Phenoxy-3-(phenyltelluro)propane (**23a**)[7] and 1-phenoxy-3-[(4-(dimethylamino)phenyl)telluro]propane (**23b**)

Chart 2



were prepared by the addition of PhTeNa and 4-$Me_2NC_6H_4TeNa$, respectively, to 1-bromo-3-phenoxypropane. Di-*n*-hexyltelluride (**24**) was prepared by the addition of 1-bromohexane to Li_2Te.[12] The mass spectra of the monotellurides displayed the characteristic isotope pattern for the Te atom (illustrated for **23b** in Figure S4, in the Supporting Information).

The rates of oxidation of monotellurides **23** and **24** were followed in the stopped-flow spectrometer under pseudo-first-order conditions. Final concentrations of 1.03×10^{-3} M telluride and 1.03×10^{-2} M H_2O_2 in MeOH at 276.8 ± 0.4 K gave observed rate constants for oxidation of $(1.10 \pm 0.01) \times 10^{-1}$ s^{-1} for **23a**, $(3.62 \pm 0.02) \times 10^{-1}$ s^{-1} for **23b**, and $(4.5 \pm 0.4) \times 10^{-1}$ s^{-1} for **24**, which correspond to second-order rate constants of 10.7 ± 0.1 M^{-1} s^{-1} for **23a**, 35.1 ± 0.2 M^{-1} s^{-1} for **23b**, and 44 ± 4 M^{-1} s^{-1} for **24**. If telluride oxidation were to remain the rate-determining step in reactions with dendrimeric telluride catalysts, then one would predict that the (dimethylamino)phenyl series and *n*-hexyl series of tellurides should be more active than the phenyl series of tellurides.

Thiol Peroxidase Activity of Organotelluride Catalysts. In our earlier work with dendrimeric organotelluride catalysts for the oxidation of halide salts with H_2O_2,[7] we employed a two-phase system of CH_2Cl_2 and pH 6 buffer, which kept the catalysts and substrate in solution. To evaluate the catalysts in a homogeneous system, the method of Tomoda et al.[8] was employed to measure thiol peroxidase activity. In this procedure, thiophenol (PhSH) is oxidized to diphenyl disulfide (PhSSPh) using H_2O_2 as the oxidant. Catalytic activity is determined by the initial rates for the oxidation of PhSH (1.0×10^{-3} M) with H_2O_2 (3.75×10^{-3} M) in MeOH in the presence of a catalyst at a standard concentration of 1.0×10^{-5} M.

A 5% CH_2Cl_2/MeOH solution of catalyst (**9**, **15**, **20**, **23**, or **24** at 2.0×10^{-5} M) and PhSH (2.0×10^{-3} M) was mixed with an equal volume of a 5% CH_2Cl_2/MeOH solution of H_2O_2 (7.5×10^{-3} M) in a stopped-flow spectrophotometer at 276.8 ± 0.4 K to give final concentrations of 1.0×10^{-5} M catalyst, 1.0×10^{-3} M PhSH, and 3.75×10^{-3} M H_2O_2. The rate of appearance of PhSSPh, with a molar extinction coefficient, ϵ, of 1.24×10^{-3} L mol^{-1} cm^{-1} at 305 nm,[8b] was monitored at 305 nm. The 5% CH_2Cl_2 was added to keep the tellurides/oxidized tellurides in solution during the course of the reaction. For hexatellurides **22**, the percentage of CH_2Cl_2 was increased to 46% (by volume) in both solutions to keep the dendrimers in solution during the time course of the analysis.

Linear increases in absorbance, k_0, were observed in the initial stages of the catalyzed reaction and are listed in Table 1 in units of ΔA s^{-1} where A is the absorbance at 305 nm. A slow, uncatalyzed background reaction was observed upon mixing the two solutions in the stopped-flow spectrometer without added catalyst. Values of k_0 were corrected for the uncatalyzed background reaction

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Table 1. Initial Rates of Oxidation (v_0) of PhSH (1×10^{-3} M) with H_2O_2 (3.75×10^{-3} M) in MeOH with Polyorganotelluride Catalysts (1×10^{-5} M) with *n* Telluride Groups from Initial Linear Increases in Absorbance (k_0)[a]

cat.	R	*n*	k_0, ΔA s^{-1} [b]	v_0, μM min^{-1}	v_0-(rel)
none		0	$(3.0 \pm 0.2) \times 10^{-6}$	0.72 ± 0.05	0.06
23a	Ph	1	$(5.3 \pm 0.4) \times 10^{-5}$	$(1.2 \pm 0.1) \times 10^{1}$	1
9a	Ph	2	$(8.8 \pm 0.5) \times 10^{-5}$	$(2.0 \pm 0.1) \times 10^{1}$	1.7
15a	Ph	3	$(1.14 \pm 0.02) \times 10^{-4}$	$(2.66 \pm 0.05) \times 10^{1}$	2.2
20a	Ph	4	$(1.81 \pm 0.05) \times 10^{-4}$	$(4.3 \pm 0.1) \times 10^{1}$	3.6
22a	Ph	6	$(4.93 \pm 0.05) \times 10^{-4}$	$(1.18 \pm 0.01) \times 10^{2}$	9.8
23b	4-$Me_2NC_6H_4$	1	$(1.06 \pm 0.05) \times 10^{-4}$	$(2.5 \pm 0.1) \times 10^{1}$	2.1
9b	4-$Me_2NC_6H_4$	2	$(1.69 \pm 0.05) \times 10^{-4}$	$(4.0 \pm 0.1) \times 10^{1}$	3.3
15b	4-$Me_2NC_6H_4$	3	$(3.15 \pm 0.03) \times 10^{-4}$	$(7.49 \pm 0.07) \times 10^{1}$	6.3
20b	4-$Me_2NC_6H_4$	4	$(3.13 \pm 0.05) \times 10^{-4}$	$(7.4 \pm 0.1) \times 10^{1}$	6.3
22b	4-$Me_2NC_6H_4$	6	$(5.6 \pm 0.1) \times 10^{-4}$	$(1.34 \pm 0.02) \times 10^{2}$	11
23	*n*-hexyl	1	$(1.53 \pm 0.09) \times 10^{-4}$	$(3.6 \pm 0.2) \times 10^{1}$	3.0
9c	*n*-hexyl	2	$(2.90 \pm 0.06) \times 10^{-4}$	$(6.9 \pm 0.1) \times 10^{1}$	5.8
15c	*n*-hexyl	3	$(4.00 \pm 0.05) \times 10^{-4}$	$(9.5 \pm 0.1) \times 10^{1}$	7.9
20c	*n*-hexyl	4	$(5.47 \pm 0.07) \times 10^{-4}$	$(1.31 \pm 0.01) \times 10^{2}$	11
22c	*n*-hexyl	6	$(1.30 \pm 0.01) \times 10^{-3}$	$(3.12 \pm 0.02) \times 10^{2}$	26

[a] Reagents were mixed in a stopped-flow spectrometer in a 2 mm cell at 276.8 ± 0.4 K, and initial rates were measured at 305 nm for the initial 5−15% of reaction. Values are the average of 7−10 independent runs with ±(standard deviation). [b] Values of k_0 were corrected for the uncatalyzed reaction prior to calculation of v_0.

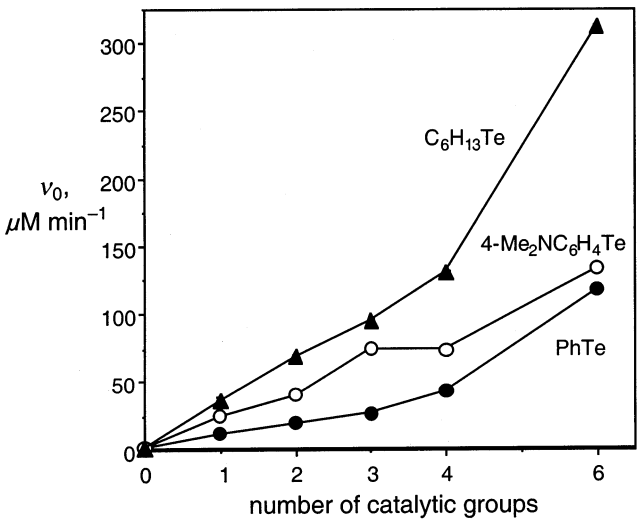

Figure 1. Plot of initial velocities, v_0, for the oxidation of thiophenol to diphenyl disulfide with hydrogen peroxide as a function of the number of organotelluride groups in polyorganotellurides for the phenyltelluro series (filled circles), [4-(dimethylamino)phenyl]telluro series (open circles), and *n*-hexyltelluro series (filled triangles). The lines connect related points and have no other significance. Standard deviations are given in Table 1.

and converted to initial velocities, v_0, in units of μM min^{-1} (Table 1). Values of v_0 as a function of the number of catalytic groups are plotted in Figure 1.

As shown in Figure 1, increasing the number of telluride groups attached to the molecular scaffold increases the catalytic activity on a molar basis along statistical lines. Stereoelectronic effects can also be imposed. In the series of molecules described here, electron-donating substituents increase the rate of oxidation of the telluride groups in the catalytic cycle, which increases overall rates of catalysis. If 1-phenoxy-3-(phenyltelluro)propane (**23a**) is assigned a relative rate of 1.0 ($v_0 = 12$ μM min^{-1}), the dendrimer catalyst **22c** with six *n*-hexyltelluro groups has a relative rate of 26 ($v_0 = 312$ μM min^{-1}) from a combination of statistical and stereoelectronic effects.

The use of dendrimeric catalysts offers potential advantages for catalyst loading on solid supports, where multiple catalytic sites can be tethered to a single site on the support. The combination of statistical and stereoelectronic effects can be used to tailor the overall catalytic activity.

Experimental Section

General Methods. Solvents and reagents were used as received from Sigma-Aldrich Chemical Co. (St. Louis, MO) unless otherwise noted. Concentration in vacuo was performed on a Büchi rotary evaporator. NMR spectra were recorded at 30.0 °C on a Varian Gemini-300, Inova 400, or Inova 500 instrument with residual solvent signal as internal standard: $CDCl_3$ (δ 7.26 for proton, δ 77.0 for carbon). Infrared spectra were recorded on a Perkin-Elmer FT-IR instrument. Elemental analyses were conducted by Atlantic Microlabs, Inc. High-resolution mass spectrometry was conducted by the Campus Chemical Instrumentation Center of The Ohio State University (Columbus, OH). Compounds **5**, **21**, **22a**, and **23a** were prepared according to ref 7. Compound **24** was prepared according to ref 13. Diphenyl ditelluride was prepared according to ref 14. Bis[(4-dimethylamino)phenyl] ditelluride was prepared according to ref 15. Dihexyl ditelluride was prepared according to ref 16.

Preparation of Methyl 3,4,5-Tris[(3-((*tert*-butyldimethylsilyl)oxy)propyl)oxy]benzoate (10). Methyl gallate (28.5 g, 155 mmol), 1-bromo-3-[(*tert*-butyldimethylsilyl)oxy]-propane (129.2 g, 0.51 mol), K_2CO_3 (96.2 g, 0.70 mol), 18-crown-6 (12.3 g, 46 mmol), and NaI (6.95 g, 46 mmol) in anhydrous acetone (1.0 L) were stirred at reflux for 48 h. The reaction mixture was concentrated. The residue was partitioned between EtOAc (0.5 L) and H_2O (1.0 L). The aqueous phase was extracted with additional EtOAc (2 × 250 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel with 50% EtOAc/hexanes as eluent to give 54.1 g (50%) of **10** as a viscous yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 2 H), 4.09 (t, 6 H, $J = 6.0$ Hz), 3.86 (s, 3 H), 3.79 (t, 6 H, $J = 6.0$ Hz), 1.99 (quint, 4 H, $J = 6.0$ Hz), 1.91 (quint, 2 H, $J = 6.3$ Hz), 0.86 (s, 27 H), 0.02 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 152.5, 142.1, 124.7, 107.8, 70.3, 65.6, 60.1, 59.5, 52.0, 33.6, 32.5, 25.9, 18.2, −5.4, −5.5; IR (film, NaCl) 1723 cm^{-1} (s); high-resolution MS (electrospray) *m*/*z* 723.4120 (calcd for $C_{35}H_{68}O_8Si_3 + Na^+$ 723.4120).

Preparation of of 3,4,5-Tris[(3-((*tert*-butyldimethylsilyl)oxy)propyl)oxy]benzyl Alcohol (11). Ester **10** (13.0 g, 18.5 mmol) and $LiAlH_4$ (0.77 g, 20 mmol) in anhydrous THF (100 mL) were stirred at 0 °C for 1 h. The reaction was quenched by the slow addition of H_2O (20 mL). The reaction mixture was concentrated to approximately half-volume and was then partitioned between EtOAc (250 mL) and water (500 mL). The aqueous phase was extracted with additional EtOAc (2 × 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to yield 10.82 g (87%) of **10** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (s, 2 H), 4.58 (d, 2 H, $J = 4.5$ Hz), 3.99−4.07 (m, 6 H), 3.76−3.82 (m, 6 H), 1.98 (quint, 4 H, $J = 6.0$ Hz), 1.91 (quint, 2 H, $J = 6.0$ Hz), 0.87 (s, 18 H), 0.86 (s, 9 H), 0.03 (s, 12 H), 0.02 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 136.9, 136.3, 104.9, 70.3, 65.4, 65.2, 60.3, 59.6, 33.5, 32.5, 25.8, 18.2, −5.4, −5.5; IR (film,

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NaCl) 3435 cm^{-1} (broad); high-resolution MS (electrospray) *m/z* 695.4178 (calcd for for $C_{34}H_{68}O_7Si_3 + Na^+$ 695.4171).

General Procedure for the Preparation of Benzoate Esters. Preparation of the Benzoate Ester 6 of 3,5-Bis-[(3-((*tert*-butyldimethylsilyl)oxy)propyl)oxy]benzyl Alcohol (5). Benzoic anhydride (1.5 equiv), pyridine (1.25 equiv), and DMAP (0.2 equiv) were dissolved in freshly distilled CH_2Cl_2 (from CaH_2, 10 mL/mmol of substrate). The benzyl alcohol (1.0 equiv) in CH_2Cl_2 (2.5 mL/mmol) was added dropwise. The reaction mixture was stirred for 16 h at ambient temperatue and was poured into H_2O, and the products were extracted with CH_2Cl_2. The organic layers were combined, dried with $MgSO_4$, and concentrated. The crude product was purified by chromatography on silica gel with 20% EtOAc/CH_2Cl_2 as eluent to give the benzoate ester.

For benzoate **6**: yield 99% as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, 2 H, J = 7.2 Hz), 7.51−7.53 (m, 1H), 7.41 (t, 2 H, J = 7.7 Hz), 6.58 (s, 2 H), 6.45 (s, 1 H), 5.28 (s, 2 H), 4.05 (t, 4 H J = 6.0 Hz), 3.79 (t, 4 H, J = 6.0 Hz), 1.97 (quint, 4 H, J = 6.0 Hz), 0.89 (s, 18 H), 0.04 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 160.2, 138.0, 132.9, 130.4, 129.6, 128.2, 106.4, 100.9, 66.5, 64.4, 59.6, 32.3, 25.8, 18.2, −5.5; IR (film, NaCl) 1723.0 cm^{-1} (s); high-resolution MS (electrospray) *m/z* 611.3198 (calcd for $C_{32}H_{52}O_6Si_2 + Na^+$ 611.3200).

For benzoate **11**: yield 99% as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d × d, 2 H, J = 1.2, 7.8 Hz), 7.52 (t, 1 H, J = 9 Hz), 7.41 (t, 2 H, J = 7.2 Hz), 6.64 (s, 2 H), 5.24 (s, 2 H), 4.09−4.02 (m, 6 H), 3.83−3.77 (m, 6 H), 2.03−1.90 (m, 6 H), 0.87 (s, 9 H), 0.9 (s, 18 H), 0.03 (s, 6 H), 0.0 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 153.0, 132.9, 131.0, 129.6, 128.3, 106.8, 70.3, 67.0, 65.6, 60.3, 58.6, 33.6, 32.57, 25.9, 25.9, 18.2, −5.3, −5.41; IR (film, NaCl) 1722.2 cm^{-1} (sharp); high-resolution MS (electrospray) *m/z* 799.4438 (calcd for $C_{41}H_{72}O_8Si_3 + Na^+$ 799.4433).

For benzoate **17**: yield 93% as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2 H, J = 8.1 Hz), 7.54 (t, 1 H, J = 7.2 Hz), 7.42 (t, 2 H, J = 7.7 Hz), 6.65 (s, 2 H), 6.54 (s, 5 H), 6.39 (s, 2 H), 5.26 (s, 2 H), 4.94 (s, 4 H), 4.02 (t, 8 H, J = 6.0 Hz), 3.77 (t, 8 H, J = 6.0 Hz), 1.94 (quint, 8 H, J = 6.0 Hz), 0.86 (s, 36 H), 0.02 (s, 24 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 160.4, 160.0, 138.8, 138.2, 132.9, 130.0, 129.7, 128.3, 106.9, 105.7, 101.6, 100.8, 70.1, 66.4, 64.5, 59.4, 32.3, 25.9, 18.2, −5.4; IR (film, NaCl) 1722.5 cm^{-1} (s); high-resolution MS (electrospray) *m/z* 1199.6417 (calcd for for $C_{64}H_{104}O_{12}Si_4 + Na^+$ 1199.6503).

General Procedure for the Desilylation of Silyl Ethers 6, 12, and 17. Hydrogen fluoride−pyridine complex (3 equiv per silyl group) was added dropwise to a solution of silyl ether in THF (10 mL per mmol). The resulting solution was stirred at ambient temperature for 16 h. The reaction mixture was partitioned between EtOAc (100 mL) and H_2O (250 mL). The aqueous phase was extracted with additional EtOAc (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was purified by chromatography on silica gel with EtOAc and then 10% MeOH/EtOAc as eluents.

For diol **7**: yield 89% of a white solid, mp 78−82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, 2 H, J = 7.0 Hz), 7.48 (t, 1 H, J = 7.0 Hz), 7.36 (t, 2 H, J = 7.7 Hz), 6.53 (d, 2 H, J = 2.0 Hz), 6.39 (t, 1 H, J = 2.0 Hz), 5.19 (s, 2 H), 4.00 (t, 4 H, J = 6.0 Hz), 3.76 (t, 4 H, J = 6.0 Hz), 3.69 (s, 2 H), 1.95 (quint, 4 H, J = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 159.9, 137.9, 132.9, 129.631, 129.4, 128.2, 106.4, 100.7, 66.4, 65.0, 59.3, 31.7; IR (KBr) 3242.7 cm^{-1} (br), 1719.7 cm^{-1} (s); high-resolution MS (electrospray) *m/z* 383.1462 (calcd for $C_{20}H_{24}O_6 + Na^+$ 383.1471).

For triol **13**: yield 92% of a white solid, mp 54−55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d × d, 2 H, J = 1.2, 8.1 Hz), 7.53 (t × t, 1 H, J = 1.2, 7.5 Hz), 7.40 (t, 2 H, J = 7.5 Hz), 6.66 (s, 2 H), 5.22 (s, 2 H), 4.16−4.07 (m, 6 H), 3.86−3.79 (m, 6 H), 3.02 (s, 3 H), 2.01 (quint, 4 H, J = 6.0 Hz), 1.93 (quint, 2 H, J = 5.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 152.4, 133.1, 131.8, 129.6, 128.4, 106.7, 71.8, 67.1, 66.8, 60.7, 60.2, 32.3, 31.8; IR (KBr) 3341.8 cm^{-1} (broad), 1721.7 cm^{-1} (sharp); high-resolution MS (electrospray) *m/z* 457.1835 (calcd for $C_{23}H_{30}O_8 + Na^+$ 457.1838).

For tetraol **18**: yield 88% as a colorless, viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2 H, J = 8.4 Hz), 7.55 (t, 1 H, J = 7.3 Hz), 7.42 (t, 2 H, J = 7.7 Hz), 6.64 (s, 2 H), 6.55 (s, 5 H), 6.40 (s, 2 H), 5.26 (s, 2 H), 4.95 (s, 4 H), 4.08 (t, 8 H, J = 6.0 Hz), 3.82 (t, 8 H, J = 5.7 Hz), 2.00 (quint, 8 H, J = 5.7 Hz), 1.80 (s, 4 H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 166.5, 161.1, 160.8, 140.1, 139.4, 133.8, 130.8, 130.1, 129.2, 107.6, 106.5, 102.239, 101.1, 70.3, 66.9, 65.5, 59.0, 33.0; IR (film, NaCl) 3381.9 cm^{-1} (br), 1717.1 cm^{-1} (s); high-resolution MS (electrospray) *m/z* 743.3041 (calcd for $C_{40}H_{48}O_{12} + Na^+$ 743.3043).

General Procedure for Conversion of (3-Hydroxypropyl)oxy Groups to (3-Bromopropyl)oxy Groups. Preparation of 3,5-Bis(3-(bromopropyl)oxy)benzyl Benzoate (8). Methanesulfonyl chloride (1.5 equiv per hydroxyl) was added dropwise over 0.5 h to a solution of alcohol and NEt_3 (1.5 equiv per hydroxyl) in THF (7 mL per mmol) at 0 °C. The solution was stirred for 2 h at 0 °C, and LiBr (4 equiv per hydroxyl, dried at 110°C for 16 h) was then added. The resulting mixture was warmed to ambient temperature, where stirring was maintained for 20 h. The reaction mixture was concentrated, the residue was partitioned between H_2O and CH_2Cl_2, and the aqueous layer was extracted with additional CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was purified via chromatography on silica gel with CH_2Cl_2 as eluent.

For dibromo compound **8**: yield 87% of a white solid, mp 85−87.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, 2 H, J = 7.2 Hz), 7.54 (t, 1 H, J = 7.3 Hz), 7.42 (t, 2 H, J = 7.5 Hz), 6.61 (d, 2 H, J = 1.8 Hz), 6.45 (s, 1 H), 5.29 (s, 2 H), 4.06 (t, 4H, J = 6.0 Hz), 3.56 (t, 4 H, J = 6.4 Hz), 2.26 (quint, 4 H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 159.7, 138.2, 132.8, 129.7, 129.4, 128.1, 106.4, 100.7, 66.1, 65.1, 32.0, 29.8; IR (KBr) 1708.2 cm^{-1} (s); high-resolution MS (electrospray) *m/z* 506.9787 (calcd for $C_{20}H_{22}Br_2O_4 + Na^+$ 506.9782).

For tribromo compound **14**: yield 62% of a white, crystalline solid, mp 53−54 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d × d, 2 H, J = 1, 7.5 Hz), 7.55 (t × t, 1 H, J = 1, 7.5 Hz), 7.43 (t, 2 H, J = 7.8 Hz), 6.68 (s, 2 H), 5.27 (s, 2 H), 4.13 (t, 4 H, J = 6 Hz), 4.06 (t, 2 H, J = 5.7 Hz), 3.68 (t, 2 H, J = 6.6 Hz), 3.61 (t, 4 H, J = 6.3 Hz), 2.33 (quint, 4 H, J = 6.0 Hz), 2.23 (quint, 2 H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 152.7, 133.1, 131.9, 129.7, 128.4, 107.2, 70.1, 66.7, 66.5, 33.5, 32.3, 30.5, 29.9; IR (KBr) 1714.7 cm^{-1}; high-resolution MS (electrospray) *m/z* 642.9280 (calcd for $C_{23}H_{27}Br_3O_5 + Na^+$: 642.9306).

For tetrabromo compound **19**: 52% as a viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, 2 H, J = 7.8 Hz), 7.56 (t, 1 H, J = 7.3 Hz), 7.44 (t, 2 H, J = 7.5 Hz), 6.71 (s, 2 H), 6.61 (d, 5 H, J = 1.2 Hz), 6.44 (s, 2 H), 5.30 (s, 2 H), 4.98 (s, 4 H), 4.06 (t, 8 H, J = 5.6 Hz), 3.57 (t, 8 H, J = 6.3 Hz), 2.27 (quint, 8 H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 159.7, 159.7, 138.9, 138.2, 132.8, 129.7, 129.4, 128.1, 106.7, 105.7, 101.4, 100.6, 69.6, 66.1, 65.1, 32.0, 29.8; IR (film, NaCl) 1716.6 cm^{-1} (s); high-resolution MS (electrospray) *m/z* 990.9653 (calcd for $C_{40}H_{44}Br_4O_8 + Na^+$ 990.9667).

General Procedure for the Preparation of Telluride Catalysts. Preparation of 3,5-Bis[(3-(phenyltelluro)-propyl)oxy]benzyl Alcohol (9a). Sodium borohydride (2 mmol per mmol of ditelluride) was added in several portions to a solution of ditelluride (1.5 equiv per bromo group) in 1 M NaOEt in ethanol (10 mL/mmol of ditelluride), and the resulting solution was stirred until the reaction mixture became colorless. The reaction mixture was added dropwise to a solution of bromo compound in THF (50 mL/mmol). The resulting mixture was heated at reflux for 20 h. The reaction mixture was concentrated, the residue was partitioned between H_2O and CH_2Cl_2, and the aqueous phase was extracted with additional CH_2Cl_2. The combined organic extracts were

dried over $MgSO_4$ and concentrated. The residue was purified via chromatography on silica gel first with CH_2Cl_2 and then with 20% EtOAc/CH_2Cl_2 as eluents.

For **9a**: yield 65% as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, 4 H, J = 7.0 Hz), 7.24 (t, 2 H, J = 7.5 Hz), 7.17 (t, 4 H, J = 7.5 Hz), 6.45, (d, 2 H, J = 2.0 Hz), 6.29 (t, 1 H, J = 2.3 Hz), 4.58 (d, 2 H, J = 6.0 Hz), 3.96 (t, 4 H, J = 5.7 Hz), 3.02 (t, 4 H, J = 7.3 Hz), 2.23 (quintet, 4 H, J = 6.5 Hz), 1.64 (t, 1 H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 143.3, 138.3, 129.2, 127.6, 111.6, 105.2, 100.6, 68.7, 65.3, 31.2, 4.2; IR (film, NaCl) 3385 cm^{-1}; high-resolution MS (electrospray) m/z 659.0061 (calcd for $C_{25}H_{28}O_3{}^{130}Te_2 + Na^+$ 659.0061).

For **9b**: yield 92% as a viscous, orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 4 H, J = 8.8 Hz), 6.52 (d, 4 H, J = 8.8 Hz), 6.38 (d, 2 H, J = 2.0 Hz), 6.28 (t, 1 H, J = 2.2 Hz), 4.54 (d, 2 H, J = 5.6 Hz), 3.93 (t, 4 H, J = 6.0 Hz), 2.92 (s, 12 H), 2.89 (t, 4 H, J = 7.2 Hz), 2.19 (quintet, 4 H, J = 6.0 Hz), 1.93 (t, 1 H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 149.9, 143.1, 140.7, 113.2, 104.7, 100.1, 94.7, 68.4, 64.7, 40.0, 30.9, 4.1; IR (film, NaCl) 3409 cm^{-1}; high-resolution MS (electrospray) m/z 723.1144 (calcd for $C_{29}H_{38}N_2O_3{}^{130}Te_2 + H^+$ 723.1085).

For **9c**: yield 62% as a viscous, orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (s, 2 H), 6.51 (s, 1 H), 4.61 (s, 2 H), 3.99 (t, 4 H, J = 6.0 Hz), 2.76 (t, 4 H, J = 7.4 Hz), 2.63 (t, 4 H, J = 7.7 Hz), 2.23−2.14 (m, 4 H), 1.75−1.64 (m, 5 H), 1.39−1.28 (m, 12 H), 0.88 (t, 6 H, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 143.3, 105.2, 100.6, 68.8, 65.3, 32.1, 31.7, 31.6, 31.1, 22.5, 14.0, 3.2, −1.9; IR (thin film, NaCl) 3399, 2955, 2923, 2855, 1597, 1455 cm^{-1}; high-resolution MS (electrospray) m/z 671.1284 (calcd for $C_{25}H_{44}O^{130}Te_2 + Na^+$ 671.1285).

For **15a**: yield 56% as a viscous, orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71−7.67 (m, 6 H), 7.26−7.21 (m, 6 H), 7.18−7.13 (m, 3 H), 6.48 (s, 2 H), 4.54 (s, 2 H), 4.01−3.88 (m, 6 H), 3.13−2.97 (m, 6 H), 2.24 (quintet, 4 H, J = 6.6 Hz), 2.15 (quintet, 2 H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 138.3, 138.2, 129.2, 129.1, 127.6, 127.4, 111.6, 105.3, 74.1, 69.8, 65.4, 32.1, 31.4, 4.9, 4.4; IR (film, NaCl) 3423.5 cm^{-1}; high-resolution MS (electrospray) m/z 916.9856 (calcd for $C_{34}H_{38}O_4{}^{130}Te_3 + Na^+$ 916.9816).

For **15b**: yield 94% as a viscous, orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.62 (d, 6 H, J = 8.8 Hz), 6.57−6.52 (t, 6 H, J = 9.4 Hz), 6.42 (s, 2 H), 4.51 (s, 2 H), 3.70−3.94 (t, 4 H, J = 6.2 Hz), 3.30−3.90 (t, 2 H, J = 8.8 Hz), 2.97−2.89 (m, 8 H), 2.94 (s, 12 H), 2.91 (s, 6 H), 2.26−2.20 (q, 4 H, J = 6.7 Hz), 2.13−2.06 (q, 2 H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 150.2, 150.1, 141.0, 140.9, 136.7, 136.2, 113.5, 113.3, 104.9, 94.9, 94.9, 74.1, 69.4, 65.3, 40.2, 32.1, 31.3, 4.9, 4.4; IR (film, NaCl) 3432, 2934, 2876, 2807, 1501, 1439, 1355, 1114 cm^{-1}; high-resolution MS (electrospray) m/z 1046.1145 (calcd for $C_{40}H_{53}N_3O_4{}^{130}Te_3 + Na^+$ 1046.1083).

For **15c**: yield 56% as a viscous, orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (s, 2 H), 4.60 (s, 2 H), 4.01 (t, 4 H, J = 6.0 Hz), 3.98 (t, 2 H, J = 6.0 Hz), 2.86−2.77 (m, 6 H), 2.66 (t, 6 H, J = 7.6 Hz), 2.24 (quintet, 4 H, J = 6.7 Hz), 2.15 (quint, 2 H, J = 6.7 Hz), 1.78−1.70 (m, 7 H), 1.37−1.26 (m, 18 H), 0.89−0.87 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 147.5, 137.1, 105.8, 74.9, 70.4, 68.8, 33.4, 32.8, 32.7, 32.4, 32.3, 32.2, 31.8, 31.7, 30.2, 23.2, 23.1, 14.6, 3.9, 3.5, −0.9, −1.2; IR (film, NaCl) 3284, 2954, 2922, 2855, 1590, 1503, 1435, 1328, 1223, 1115 cm^{-1}; high-resolution MS (electrospray) m/z 947.1694 (calcd for $C_{34}H_{62}O_4{}^{130}Te_3 + Na^+$ 947.1733).

For **20a**: yield 72% as an orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, 8 H, J = 7.2 Hz), 7.14−7.27 (m, 12 H), 6.60 (s, 2 H), 6.51 (d, 5 H, J = 1.5 Hz), 6.32 (s, 2 H), 4.93 (s, 4 H), 4.61 (s, 2 H), 3.96 (t, 8 H, J = 5.9 Hz), 3.02 (t, 8 H, J = 7.4 Hz), 2.23 (quint, 8 H, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.05, 160.0, 143.4, 139.1, 138.3, 129.1, 127.6, 111.6, 105.8, 105.7, 101.3, 100.8, 69.9, 68.7, 65.2, 31.2, 4.2; IR (film, NaCl) 3442.9 cm^{-1}; high-resolution MS (electrospray) m/z 1399.0520 (calcd for $C_{57}H_{60}O_7{}^{130}Te_4 + Na^+$ 1399.0486).

For **20b**: yield 92% as an orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.62 (d, 8 H, J = 8.8 Hz), 6.55−6.50 (m, 12 H), 6.32 (s, 2 H), 4.94 (s, 4 H), 4.62 (s, 4 H), 3.97−3.94 (t, 8 H, J = 6.0 Hz), 2.93−2.87 (m, 8 H), 2.90 (s, 24 H), 2.22−2.16 (q, 8 H, J = 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 159.5, 149.9, 148.6, 140.8, 138.8, 129.1, 113.0, 105.5, 105.2, 100.7, 100.4, 94.4, 69.5, 68.5, 39.9, 30.9, 4.0; IR (film, NaCl) 3437, 2921, 2873, 2897, 1590, 1501, 1446, 1354, 1196, 1061 cm^{-1}; high-resolution MS (electrospray) m/z 1571.2155 (calcd for $C_{65}H_{80}N_4O_7{}^{130}Te + Na^+$ 1571.2174).

For **20c**: yield 51% as an orange oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (s, 2 H), 6.53 (s, 1 H), 6.41 (s, 2 H), 4.96 (s, 4 H), 4.64 (d, 2 H, J = 5.0 Hz), 4.00 (t, 8 H, J = 6.0 Hz), 2.77 (t, 8 H, J = 7.3 Hz), 2.64 (t, 8 H, J = 7.6 Hz), 2.22−2.17 (m, 8 H), 1.76−1.70 (m, 9 H), 1.37−1.27 (m, 24 H), 0.89−0.86 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 160.1, 143.4, 139.1, 105.8, 105.7, 101.3, 100.8, 70.0, 68.8, 65.3, 32.1, 31.7, 31.6, 31.1, 22.5, 14.0, 3.3, −1.9; IR (film, NaCl) 3228, 2954, 2923, 2855, 1597, 1455, 1377, 1115 cm^{-1}; high-resolution MS (electrospray) m/z 1425.3117 (calcd for $C_{57}H_{92}O_7{}^{130}Te_4 + Na^+$ 1425.3120).

For **22b**: yield 82% as an orange oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, 12 H, J = 9 Hz), 6.98 (d, 6 H, J = 9 Hz), 6.84 (d, 6 H, J = 9 Hz), 6.53 (d, 12 H, J = 9 Hz), 6.51 (s, 6 H), 6.32 (s, 3 H), 4.92 (s, 6 H), 3.95 (t, 12 H, J = 6 Hz), 2.92 (s, 36 H), 2.88 (t, 12 H, J = 6 Hz), 2.18 (quintet, 12 H, J = 6 Hz), 2.08 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 156.8, 150.3, 142.0, 141.1, 139.3, 129.6, 113.9, 113.3, 105.8, 100.7, 94.6, 69.9, 68.8, 50.6, 40.2, 31.2, 4.1 (one overlapped peak). Anal. Calcd for $C_{107}H_{126}N_6O_9Te_6$: C, 53.42; H, 5.28; N, 3.49. Found: C, 53.50; H, 5.31; N, 3.24.

For **22c**: yield 42% as an orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, 6 H, J = 8.6 Hz), 6.87 (d, 8 H, J = 8.6 Hz), 6.58 (s, 6 H), 6.41 (s, 3 H), 4.96 (s, 6 H), 4.01 (t, 12 H, J = 6.3 Hz), 2.78 (t, 12 H, J = 7.3 Hz), 2.65 (t, 12 H, J = 7.3 Hz), 2.21 (quint, 12 H, J = 6.3 Hz), 2.12 (s, 3 H), 1.74 (quint, 12 H, J = 7.3 Hz), 1.39−1.29 (m, 36 H), 0.90−0.87 (m, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 156.6, 141.8, 139.3, 129.5, 113.8, 105.7, 100.6, 69.8, 68.7, 50.5, 32.0, 31.6, 31.5, 31.0, 30.6, 22.4, 14.0, 3.1, −2.0; IR (film, NaCl) 2954, 2923, 2868, 1598, 1507, 1457, 13787, 1244, 1178 cm^{-1}. Anal. Calcd for $C_{95}H_{144}O_9Te_6$: C, 51.96; H, 6.61. Found: C, 52.11; H, 6.53.

Preparation of 1-Phenoxy-3-[(4-(dimethylamino)phenyl)telluro]propane (23b). *t*-BuLi (12 mL of a 1.7 M solution, 20 mmol) was added dropwise to a solution of 4-bromo-*N*,*N*-dimethylaniline (2.00 g, 10 mmol) in THF (40 mL) at −78 °C. The resulting solution was stirred at −78 °C for 1 h and was then warmed to ambient temperature. Tellurium powder (1.28 g, 10 mmol) was added in one portion, and the resulting mixture was stirred at room temperature for 1 h. 1-Bromo-3-phenoxypropane (2.04 g, 9.5 mmol) in 5 mL of THF was added, and the resulting mixture was heated at reflux for 16 h. The reaction mixture was filtered through Celite, and the filter cake was washed with CH_2Cl_2 (50 mL). The filtrate was concentrated, and the residue was partitioned between H_2O (100 mL) and CH_2Cl_2 (50 mL). The aqueous layer was extracted with additional CH_2Cl_2 (3 × 25 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. The crude product was then purified by column chromatography on silica gel with 60% CH_2Cl_2/hexanes as eluent to give 1.9 g (52%) of **23b** as an orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, 2 H, J = 8.8 Hz), 7.24 (t, 2H, J = 7.8), 6.91 (t, 1 H, J = 7.2), 6.84 (d, 2 H, J = 8.0 Hz), 6.54 (d, 2 H, J = 8.8 Hz), 3.97 (t, 2 H, J = 6.0 Hz), 2.94 (s, 6 H), 2.90 (t, 2 H, J = 7.4 Hz), 2.20 (quint, 2 H, J = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 150.3, 141.2, 129.4, 120.6, 114.5, 113.4, 94.7, 68.7, 40.2, 31.2, 4.3; high-resolution MS (EI) m/z 385.0694 (calcd for $C_{17}H_{21}NO^{130}Te$ 385.0681). Anal. Calcd for $C_{17}H_{21}NOTe$: C, 53.32; H, 5.53; N, 3.66. Found: C, 53.26; H, 5.61; N, 3.32.

Stopped-Flow Experiments. All stopped-flow experiments were performed on a SX18 Stopped-Flow Spectrometer (Applied Photophysics, Leatherhead, U.K.). The sample-

handling unit was fitted with two drive syringes that are mounted inside a thermostated-bath compartment, which allowed for variable-temperature experimentation. The optical detection cell was set up in the 2 mm path length. First- and second-order curve fitting and rate constants used a Marquardt algorithm[17] based on the routine Curfit.[18]

Preparation of Stock Solutions for Catalysis Experiments. Stock solutions of 2.0×10^{-3} M catalyst in CH_2Cl_2 and 5.0×10^{-2} M PhSH in CH_2Cl_2 were prepared. These were diluted with MeOH to give a 5% CH_2Cl_2/MeOH solution of 2.0×10^{-5} M telluride and 2.0×10^{-3} M PhSH. A stock solution of 7.50×10^{-3} M H_2O_2 in MeOH was prepared. These two solutions were mixed in the stopped-flow spectrometer to give concentrations of 1.0×10^{-5} M telluride, 1.0×10^{-3} M PhSH, and 3.75×10^{-3} M H_2O_2, and the increase in absorbance at 305 nm was measured. The concentration of H_2O_2 in the stock solution was determined from the absorbance at 240 nm ($\epsilon = 43.6\ cm^{-1}\ M^{-1}$).[19] The values in Table 1 are the average of 7−10 independent runs (±(standard deviation)).

Preparative Reaction for PhSSPh. Thiophenol (0.11 g, 1.0 mmol) was dissolved in 20 mL of MeOH, and H_2O_2 (0.5 mL of an 8.5 M[18] solution, 4.3 mmol) was added. Di-*n*-hexyl telluride (0.010 g, 0.03 mmol) was added, and the resulting solution was stirred for 1 h at ambient temperature. The reaction mixture was concentrated, and the residue was partitioned between 20 mL of water and 20 mL of CH_2Cl_2. The organic phase was dried over $MgSO_4$ and concentrated. The residual oil was purified via recrystallization from hexanes to give 0.066 g (50%) of PhSSPh, mp 57−59 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 4 H, $J = 7.2$ Hz), 7.38 (t, 4 H, $J = 7.4$ Hz), 7.32 (t, 2 H, $J = 7.2$ Hz).

Oxidation of Tellurides 23 and 24. Stock solutions of 2.06×10^{-3} M telluride and 2.06×10^{-2} M H_2O_2 in 5% CH_2Cl_2/MeOH were prepared. These two solutions were mixed in the stopped-flow spectrometer to give concentrations of 1.03×10^{-3} M telluride and 1.03×10^{-2} M H_2O_2, and the increase in absorbance at 325 nm for **23a**, 350 nm for **23b**, and 352 nm for **24** was measured as a function of time for 7−10 independent runs (±(standard deviation)).

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Supporting Information Available: Figure S1, showing the parent ion isotope cluster in the mass spectrum of **9a**, Figure S2, showing the parent ion isotope cluster in the mass spectrum of **15c**, Figure S3, showing the parent ion isotope cluster in the mass spectrum of **20a**, Figure S4, showing the parent ion isotope cluster in the mass spectrum of **23b**, and ^{1}H NMR spectra for polyorganotellurides **9**, **15**, **20**, and **22**. This information is available free of charge via the Internet at http://pubs.acs.org.

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