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# Arylthiols as Highly Chemoselective and Environmentally Benign Radical Reducing Agents

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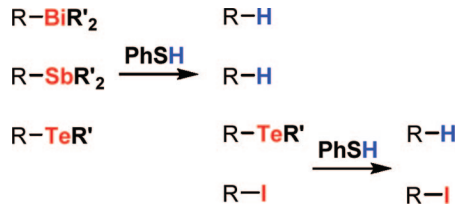
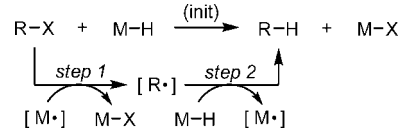



Arylthiols serve as excellent environmentally benign reducing agents for organotellurium, organostibine, and organobismuthine compounds under radical conditions. Both small molecules and macromolecules possessing these heteroatom groups are reduced under moderate thermal conditions to give near quantitative yields in most cases. The reduction shows high chemoselectivity with respect to the heteroatom compounds; the reactivity decreases in the order alkylbismuthines, alkylstibines, and alkyltellurides, while simple alkyl iodides could not be reduced. Alkyltellurides are selectively reduced in the presence of alkyl iodides even when an excess amount of arylthiol is used. Furthermore, alkylstibines are also selectively reduced in the presence of alkyltellurides. Moreover, the reduction conditions are compatible with the presence of a variety of polar functional groups in the substrates, products, and solvents, which are not tolerant under ionic and metal-catalyzed conditions. Carbon−carbon bond formation is possible with use of the carbon-centered radicals that are generated. The results clearly reveal the synthetic utility of arylthiols in organic synthesis.

## Introduction

The radical-mediated reduction of organoheteroatom compounds (R−X), such as organohalogens and organochalcogens, has been widely used in organic synthesis (Scheme 1).[1−4] Tributyltin hydride (M = $SnBu_3$) has been most extensively used for this purpose because it readily donates hydrogen to carbon-centered radicals giving reduction products (step 2). Furthermore, the high reactivity of the resulting tin radical allows heteroatoms to be abstracted from organochalcogens or organohalides to generate carbon-centered radicals (step 1) in a radical chain reaction.[5,6]

**SCHEME 1. Radical-Mediated Reduction of Organoheteroatom Compounds by Metal Hydride**




However, the development of alternative reducing agents is strongly desired because of the environmental concerns involved in using organotin compounds.[3,7] For this reason alternative reducing agents such as tris(trimethylsilyl)silane[8] and hydrogen

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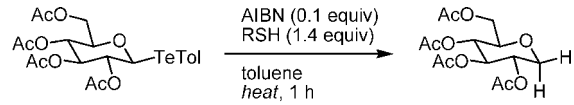
phosphates[9,10] have been developed, and a search for new and efficient reducing agents possessing metal−hydrogen bonds, such as Ge−H,[11−13] Ga−H,[14] In−H,[15] Zr−H,[16,17] and Cr−H,[18] is ongoing.[19,20]

Thiols are excellent hydrogen donors in radical reactions, but their use in the reduction of organohalogens has so far been unsuccessful due to the poor reactivity of thiyl radicals toward the abstraction of halogen atoms (step 1).[21] Therefore, thiols can reduce organohalogens only in the presence of silanes as polarity reversal catalysts[22−24] or by using silylthiols,[25,26] thus their synthetic applications have been limited.

In contrast, we have recently reported that benzenethiol is able to reduce tellanylglycoside **1** with high efficiency under photoirradiation.[27] The reaction of organostibines and bismuthines with benzenethiol to give phenylthiostibines and bismuthines has also been reported.[28] Although the fate of the carbon residues derived from the organostibines and bismuthines was not described in this study, it is probable that the reduction products were formed.

Despite these results, the synthetic efficiencies of thiols as reducing agents for organoheteroatom compounds are still unknown. These studies prompted us to examine the versatility of the thiol reduction of various organoheteroatom compounds including organotellurides,[29−48] organostibines,[49,50] and organobismuthines[51] under thermal conditions. These heteroatom compounds have recently been recognized as excellent precursors of carbon-centered radicals for the precision synthesis of both small molecules and macromolecules. The development of mild and environmentally benign reducing agents would greatly facilitate the use of these heteroatom compounds in organic and polymer synthesis.

**TABLE 1. Reduction of Tellanylglycoside 1 with Various Thiols**




**1** **2**

| run | RSH | temp (°C) | yield (%)[a] |
|---|---|---|---|
| 1 | PhSH | 80 | 88 (100) |
| 2 | *p*-$MeC_6H_4SH$ | 80 | 85 (100) |
| 3 | *p*-$MeOC_6H_4SH$ | 80 | 79 (100) |
| 4 | *p*-$HOC_6H_4SH$ | 80 | 74 (100) |
| 5 | *p*-$ClC_6H_4SH$ | 80 | 83 (100) |
| 6 | *p*-$CF_3C_6H_4SH$ | 80 | 72 (100) |
| 7 | *p*-$NO_2C_6H_4SH$ | 80 | 56 (100) |
| 8 | $C_6F_5SH$ | 80 | 79 (100) |
| 9 | *n*-$C_8H_{17}SH$ | 80 | 67 (100) |
| 10[b] | PhSH | 100 | 94 (100) |
| 11[c] | PS-thiophenol | 85 | 98 (100) |

[a] Determined by $^1H$ NMR. The number in parentheses is the yield based on the amount of **1** converted. [b] PhSH (2 equiv) was used in the presence of ACHN [1,1-azobis(cyclohexane-1-carbonitrile)] instead of AIBN. The 10-h half-life decomposition temperatures of ACHN and AIBN are 88 and 65 °C in toluene, respectively. [c] Five equivalents of polymer-supported thiophenol [3-(3-mercaptophenyl)propaneamidomethyl polystyrene] was used.

## Results and Discussion

The substituent effect of thiols in the reduction was examined with tellanylglycoside **1** as a model substrate (Table 1). A solution of **1**, AIBN (0.1 equiv), and benzenethiol (1.4 equiv) was heated in toluene at 80 °C for 1 h, and the desired product **2** was formed in 88% yield together with a 12% recovery of **1**, as determined by $^1H$ NMR (Table 1, run 1). The reduction proceeded smoothly in various nonpolar and polar solvents including trifluoromethylbenzene, dimethyl formamide, propionitrile, and 2-butanone. Arylthiols with both electron-donating and withdrawing substituents at the para-position of the aryl group tended to decrease the reactivity more than benzenethiol

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**SCHEME 2. Formation and Stability of Phenyl(*p*-tolyltellanyl)sulfane**


**TABLE 2. Reduction of Organoheteroatom Compounds with Benzenethiol[a]**

| run | substrate | azo initiator[b] | PhSH (equiv) | conditions (°C/h) | product | yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 | *n*-$C_{12}H_{25}$TePh | V-30 | 5.0 | 120/2 | *n*-$C_{12}H_{26}$ | 37 |
| 2 | *i*-PrTePh (**3**) | ACHN | 2.0 | 100/5 | *i*-PrH | 99 |
| 3 | *t*-BuTePh (**4**) | none | 1.2 | 30/1 | *t*-BuH | 100 |
| 4 | PhCH(Me)TeMe | none | 1.2 | 30/1 | PhEt | 100 |
| 5 | $Me_2C(CO_2Et)$TeMe | none | 1.2 | 30/1 | $Me_2CHCO_2Et$ | 100 |
| 6 | $Me_2C(CN)$TeMe (**5**) | AIBN | 1.2 | 80/1 | $Me_2CHCN$ | 100 |
| 7 | PhCOTeMe | ACHN | 5.0 | 100/5 | PHCHO | 95 |
| 8 | $(n\text{-}C_{12}H_{25})_3Sb$ | AIBN | 3.5 | 80/0.5 | *n*-$C_{12}H_{26}$ | 296[d] |
| 9 | *i*-$Pr_3Sb$ (**6**) | AIBN | 3.5 | 80/0.5 | *i*-PrH | 295[d] |
| 10 | $Me_2C(CO_2Et)SbMe_2$ | none | 1.1 | 30/1 | $Me_2CHCO_2Et$ | 100 |
| 11 | $Me_2C(CN)$ $SbMe_2$ | none | 1.2 | 80/8 | $Me_2CHCN$ | 99 |
| 12 | $(t\text{-}BuC_6H_4)_3Sb$ | V-30 | 5.0 | 120/5 | t-BuPh | <6 |
| 13 | $Me_2C(CO_2Me)BiMe_2$ | none | 1.1 | 30/1 | $Me_2CHCO_2Et$ | 100 |
| 14 | $Me_2C(CN)$ $BiPh_2$ | none | 1.1 | 80/5 | $Me_2CHCN$ | 100 |
| 15 | $(t\text{-}BuC_6H_4)_3Bi$ | V-30 | 5.0 | 120/5 | *t*-BuPh | 288[d] |
| 16 | $EtOCOCH_2I$ | AIBN | 1.4 | 80/2 | $EtOCOCH_3$ | 100 |

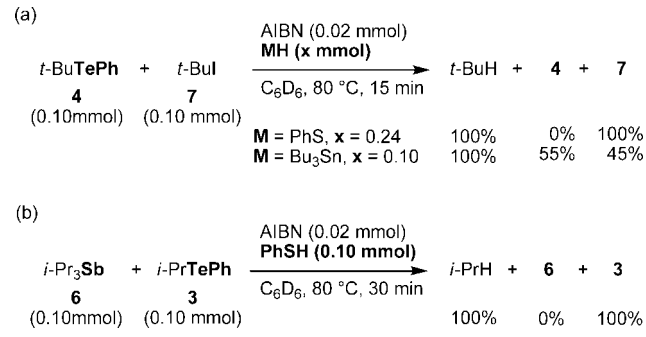
[a] The reaction was carried out by heating a solution of the substrate with benzenethiol in the presence or absence of an azo-initiator (0.1 equiv) in $C_6D_6$ or toluene. [b] V-30: 2-(carbamoylazo)isobutyronitrile. The 10-h half-life decomposition temperature of V-30 is 104 °C in toluene. [c] Determined by $^1H$ NMR or GLC. [d] Yield based on an assumption that 1 mol of substrate generates 3 mol of reduction products.

(runs 2−8). Because the rate-determing step is the abstraction of the tolyltellanyl group by the thiyl radical (step 1 in Scheme 1), this step is slightly affected by the electronic effects. An alkylthiol also showed lower reactivity than benzenethiol (run 9). Better results occurred with the use of 2 equiv of benzenethiol at 100 °C (run 10). Polymer-supported thiophenol was also effective and gave **2** in quantitative yield (run 11).

The reduction by benzenethiol also generated a byproduct, which was tentatively identified as phenyl(*p*-tolyltellanyl)sulfane by $^1H$ NMR spectroscopy in an experiment carried out in $C_6D_6$. However, this compound is thermally labile and underwent disproportionation to ditolyl ditelluride and diphenyl disulfide (Scheme 2). Equilibrium was finally reached, at which the solution contained a 25:75 ratio of the tellanylsulfane and the ditelluride/disulfide mixture. The ditelluride and disulfide were both isolated in pure form by silica gel chromatography, but attempts to isolate the tellanylsulfane were unsuccessful because it is unstable under the chromatography conditions.

The synthetic scope of the thiol reduction was examined by using various organoheteroatom compounds with benzenethiol, and the results are summarized in Table 2. The required reaction conditions strongly depend on the stability of the carbon-centered radicals that are liberated from the substrates. Thus, while the reduction of simple primary alkyl tellurides was slow and did not complete within a reasonable period of time even with 5 equiv of benzenethiol (Table 2, run 1), secondary alkyl tellurides were reduced almost quantitatively at 100 °C with 2 equiv of benzenethiol (run 2). The reduction of simple *tert*-alkyl tellurides and of tellurides possessing a radical-stabilizing group at the α-carbon position took place quantitatively even at room temperature in the absence of AIBN (runs 3−6). We could not observe the formation of benzene derived from the reduction of benzenetellanyl group (runs 1 and 2). Therefore,

**SCHEME 3. Chemoselectivity of Thiol Reduction**




$sp^2$ carbon−tellurium bonds in aryltellurides are inert under these conditions, and selective and quantitative reduction of the $sp^3$ carbon−tellurium bond occurred. An acyl telluride, which possesses an $sp^2$ carbon−tellurium bond yet liberates a stabilized acyl radical, was efficiently reduced to the corresponding aldehyde (run 7). Polar functional groups in the substrates and/or products, such as aldehyde, ester, and cyano groups, were not affected because the reaction proceeded under neutral conditions.

We next examined the reduction of organostibines and organobismuthines, and found that these heteroatom compounds were also excellent substrates (Table 2, runs 8−15). It should be noted that the thiol reduction of these compounds takes place much faster than that of organotellurium compounds. Thus, both primary and secondary alkylstibines were reduced at 80 °C. All of the $sp^3$ carbon−antimony bonds in trialkylstibines were reduced virtually quantitatively (runs 8 and 9). *tert*-Alkyl−antimony bonds were also effectively reduced at 30−80 °C. The reduction occurred selectively at the carbon−antimony bond to liberate most stable radicals when unsymmetrical substrates were used, and gave the reduction products in quantitative yields by employing 1 equiv of benzenethiol (runs 10 and 11). *tert*-Alkyl−bismuth bonds were also reduced quantitatively under mild conditions (runs 13 and 14). The aryl−antimony bond could not be reduced even at 120 °C (run 12), but the aryl−bismuth bond was reduced quantitatively under the same conditions (run 15). While simple alkyl iodides were shown to be completely inert in benzenethiol (vide infra), an iodide possessing a radical-stabilizing ester group at the α-carbon position was successfully reduced in quantitative yield (run 16).

The high chemoselectivity of the current reduction process should be emphasized. Benzenethiol was completely unable to reduce *tert*-butyl iodide (**7**), *tert*-butyl bromide, or *tert*-butyl phenyl selenide under similar conditions. Indeed, a competition experiment in which the reduction of a mixture of *tert*-butyl phenyl telluride (**4**) and **7** was attempted resulted in the selective reduction of **4**, even when 2 equiv of benzenethiol was employed. Iodide **7** was recovered completely intact (Scheme 3a). In contrast, the same competition experiment with 1 equiv of tributyltin hydride took place nonselectively, leaving equal amounts of unreacted **4** and **7**. A competition experiment involving *tri*-isopropylstibine (**6**) and isopropyl phenyl telluride (**3**) resulted in the selective reduction of **6** (Scheme 3b). These results indicate that thiols can be used as highly chemoselective reducing agents.

The above results clearly indicate that the reactivity of the organoheteroatom compounds decreases in the order bismuthines, stibines, tellurides, and iodides. This order of reactivity is

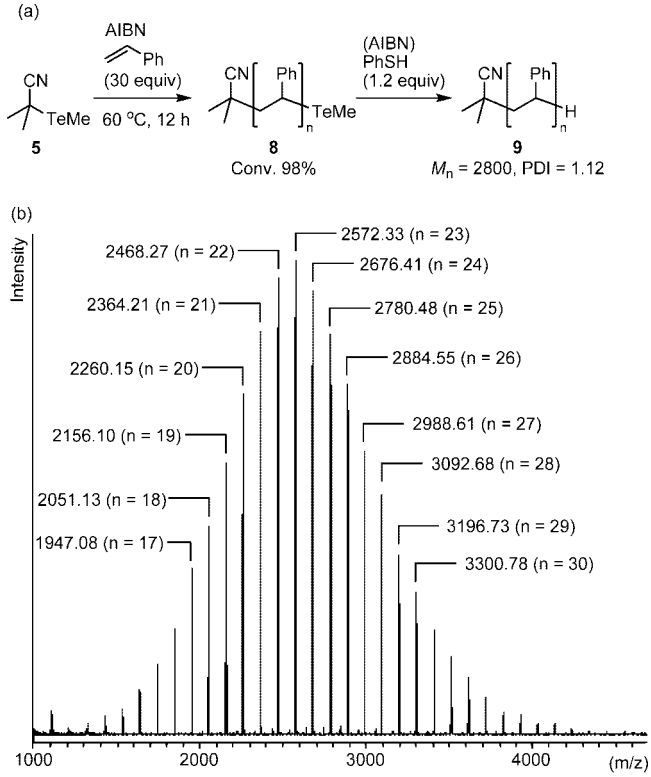



**FIGURE 1.** (a) Synthesis and (b) TOF-MS spectrum of $\omega$-end-reduced polystyrene **8**. Molecular ion mass, as indicated by the average mass number, is observed as the silver ion-added form $(M + Ag)^+$. The MS analysis indicated 1.4% formation of $\alpha,\omega$-(2-cyano-2-propyl)-substituted polystyrene, which formed by the coupling of the polymer-end radical with 2-cyano-2-propyl radical generated from AIBN.

identical with that observed in the homolytic substitution reaction of heteroatom compounds with carbon-centered radicals obtained experimentally[45,51,52] and computationally,[49,53] and is consistent with the rate-determining step of the reduction being the abstraction of the heteroatom from the substrate (step 2 in Scheme 1). However, the difference in reactivity toward carbon-centered radicals is relatively small (the reactivity differs by no more than ten times),[49,51,52] and further investigation is required to clarify the origin of the extremely large difference in reactivity with respect to reduction.

The synthetic utility of the thiol reduction was further examined by carrying out the reduction of the heteroatom group of a polymer end. Polystyrene **8** bearing a methyltellanyl group at the $\omega$-end of the polymer was prepared from organotellurium compound **5** and 30 equiv of styrene in the presence of AIBN (Figure 1a).[45] It was reduced with benzenethiol (1.2 equiv) at 80 °C for 1 h to give end-protonated polystyrene **9** with $M_n$ = 2800 and PDI = 1.12, where $M_n$ is the number-average molecular weight and PDI is the polydispersity index obtained by the gel permeation chromatography analysis. When matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy was carried out on **9**, the selective formation of end-reduced polystyrene was revealed (Figure 1b). In view of the apparently high reactivities of organostibines and bismuthines, we expect that polymer end groups possessing these heteroatoms would also be reduced by benzenethiol.

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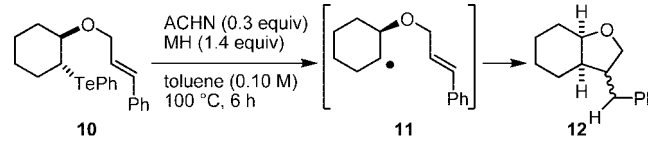
**SCHEME 4. Reductive Intramolecular Cyclization**




To verify the reaction mechanism, intramolecular cyclization was examined by using the organotellurium compound **10** (Scheme 4).[40] When **10** was treated with benzenethiol in the presence of 1,1′-azobis(cyclohexane-1-carbonitrile) (ACHN), the cyclized product **12** was formed in 86% yield with complete *cis*-selectivity with respect to the ring junction and with 1:2.3 *endo*/*exo* selectivity for the benzilic position. The selectivity was identical with that obtained from the tributyltin hydride-promoted cyclization of **10** within an experimental error with an *endo*/*exo* ratio of 1:2.2. These results clearly indicate that the thiol reduction also proceeds via radical intermediate **11**.

## Conclusion

Arylthiols serve as excellent reducing agents for organotellurium, stibine, and bismuthine compounds. The mild reaction conditions, high yields, and high chemoselectivity of this reduction method suggest that it will find many synthetic applications in radical-mediated synthetic transformations.

## Experimental Section

**Typical Experimental Procedure for the Reduction of Tellanyl Glycoside 1: Synthesis of 1-Deoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranoside (2).**[54] Benzenethiol (30.9 mg, 0.28 mmol) was added to a solution of **1**[55] (110.0 mg, 0.20 mmol) and AIBN (3.3 mg, 0.02 mmol) in toluene (0.6 mL) under a nitrogen atmosphere, and the resulting reaction mixture was heated at 80 °C for 1 h. The solvent was removed in vacuo, and $CDCl_3$ and 1,1,2,2-tetrachloroethane (10.5 $\mu$L; an internal standard) were introduced. The reduction product **2** was formed in 88% yield together with a 12% recovery of **1**, as determined by $^1$H NMR analysis. The pure product **2** was obtained by flash chromatography on silica gel, using 35% ethyl acetate/hexane as an eluent. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.02−2.05 (m, 9 H), 2.10 (s, 3 H), 3.31 (t, $J$ = 10.8 Hz, 1 H), 3.60 (ddd, $J$ = 10.0, 4.8, 2.4 Hz, 1 H), 4.13 (dd, $J$ = 12.8, 2.4 Hz, 1 H), 4.16 (dd, $J$ = 11.2, 5.6 Hz, 1 H), 4.21 (dd, $J$ = 12.4, 4.8 Hz, 1 H), 5.02 (ddd, $J$ = 10.4, 10.0, 5.6 Hz, 1 H), 5.04 (t, $J$ = 9.6 Hz, 1 H), 5.21 (t, $J$ = 9.6 Hz, 1 H).

**Typical Experimental Procedure for the Reduction When a Volatile Product Is Generated: Reduction of Isopropylphenyltelluride (3).** A solution of **3** (49.6 mg, 0.20 mmol), benzenethiol (44.1 mg, 0.40 mmol), and ACHN (4.9 mg, 0.02 mmol) in $C_6D_6$ (0.6 mL) was heated at 100 °C for 5 h in a sealed NMR tube. The $^1$H NMR analysis indicated the complete disappearance of **3** and the formation of propane in 99% yield. $^1$H NMR (400 MHz, $C_6D_6$) 0.85 (t, $J$ = 7.2 Hz, 6 H), 1.25 (sept, $J$ = 7.2 Hz, 2 H).

**Synthesis of End-Reduced Polystyrene 9.** Polystyrene **8** was prepared by heating a solution of **5** (21.1 mg, 0.10 mmol), AIBN (16.9 mg, 0.10 mmol), and styrene (312.5 mg, 3.0 mmol) at 60 °C for 12 h under a nitrogen atmosphere in a glovebox.[45] A small portion of the reaction mixture was withdrawn and dissolved in $CDCl_3$. The conversion of the monomer (98%) was determined by

(54) Beckwith, A. L. J.; Duggan, P. J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1673–1679.
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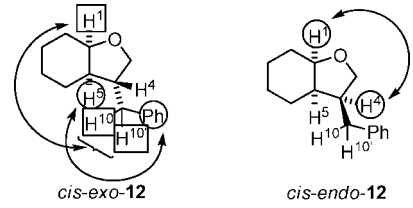
$^1$H NMR. Trifluoromethylbenzene (1.0 mL) was added to the rest of the reaction mixture, which was shaken until it became a homogeneous solution. Benzenethiol (13.2 mg, 0.12 mmol) was added, and the resulting mixture was heated at 80 °C for 2 h. The mixture was poured into methanol (200 mL) with vigorous stirring. The precipitate was collected by filtration and dried under reduced pressure at 40 °C to give 280.1 mg of polystyrene (90% yield). Analytical GPC indicated that the polymer formed with $M_n = 2800$ and PDI = 1.12. The MALDI-TOF MS analysis indicated the formation of the end-protonated polystyrene with $M_n = 2600$ and PDI = 1.04.

***trans*-2-Phenyltellanylcyclohexyl Cinnamyl Ether (10).** Sodium hydride (0.56 g, 60% mineral oil dispersion, 14 mmol) was placed in a dry, two-necked round-bottomed flask, which was flushed with nitrogen. The mineral oil was washed off by adding anhydrous hexane (2 mL), which was withdrawn after stirring. This procedure was repeated three times. Anhydrous THF (30 mL) and 2-hydroxycyclohexyl phenyl telluride[56] were added at room temperature, and the resulting mixture was stirred for approximately 2 h at room temperature. (*E*)-Cinnamyl bromide (2.37 g, 12 mmol) was added, and the resulting solution was stirred for 14 h. Water was added, and the organic phase was extracted with hexane. The combined organic phase was washed with saturated aqueous $NH_4Cl$ solution and saturated aqueous NaCl solution, dried over $MgSO_4$, and filtrated. The solvent was removed in vacuo, and the residue was purified by flash chromatography (2% ethyl acetate/hexane followed by 5% ethyl acetate/hexane) to afford 3.40 g (81%) of **10** as a light yellow oil. IR (neat) 693, 735, 968, 1075, 1020, 1433, 1447, 1575, 2860, 2940, 3030, 3070; HRMS (EI) *m/z* calcd for $C_{21}H_{24}OTe$ $(M)^+$, 422.0889, found 422.0910; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.14−1.38 (m, 3 H), 1.48−1.62 (m, 2H), 1.75−1.86 (m, 1H), 1.90−2.00 (m, 1 H), 2.11−2.22 (m, 1 H), 3.48 (dt, $J$ = 9.2, 4.0 Hz, 1 H), 3.60 (ddd, $J$ = 10.8, 9.2, 4.0 Hz, 1 H), 4.12 (ddd, $J$ = 12.8, 6.0, 1.2 Hz, 1 H), 4.30 (ddd, $J$ = 12.8, 6.0, 1.2 Hz, 1 H), 6.29 (dt, $J$ = 16.0, 6.0 Hz, 1 H), 6.60 (d, $J$ = 16.0 Hz, 1 H), 7.14−7.35 (m, 6 H), 7.37−7.43 (m, 2 H), 7.80−7.86 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 24.0 ($CH_2$), 27.4 ($CH_2$), 32.2 (OCH), 32.3 ($CH_2$), 33.8 ($CH_2$), 69.3 ($OCH_2$), 82.5 (TeCH), 111.3 (TeC), 126.5 (CH), 127.5 (CH), 127.8 (CH), 128.4 (CH), 128.8 (CH), 131.9 (CH), 136.7 (C), 140.8 (CH).

**4-Benzyl-2-oxabicyclo[3.4.0]nonane (12).** Benzenethiol (30.9 mg, 0.28 mmol) was added to a solution of **10** (84.0 mg, 0.20 mmol) and ACHN (4.9 mg, 0.02 mmol) in toluene (2.0 mL) under a nitrogen atmosphere, and the resulting reaction mixture was heated at 100 °C for 6 h. ACHN (9.8 mg, 0.04 mmol) was added in two portions (0.02 mmol each after 2 and 4 h) during the reaction. The solvent was removed in vacuo, and $CDCl_3$, hexadecane (10.0 $\mu$L, an internal standard for GC analysis), and 1,1,2,2-tetrachloroethane (10.5 $\mu$L, an internal standard for $^1$H NMR analysis) were added. The cyclized product **12** formed as a 1:2.3 mixture of two isomers as determined by the GC analysis, and **10** was recovered in 14% yield as determined by the $^1$H NMR analysis. Purification by flash chromatography (5% ethyl acetate/hexane) followed by preparative-recycling GPC afforded **11** as a 1:2.2 mixture in 86% yield (185.1 mg). The same experiment performed with $Bu_3SnH$ instead of PhSH gave **11** in 88% yield as a 1:2.2 mixture of *endo* and *exo* isomers by the GC analysis. IR (neat) 705, 760, 920, 940, 1030, 1060, 1460, 1500, 1720, 2870, 2940; HRMS (GC-MS, EI) *m/z* calcd for $C_{15}H_{20}O$ $(M)^+$, 215.1436, found 215.1430 (*endo*), 215.1430 (*exo*); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.06−1.42 (m, 3.0 H), 1.41−1.64 (m, 3.7 H), 1.68−1.90 (m, 2.0 H), 1.93−2.01 (m, 0.3 H, *endo*), 2.24−2.34 (m, 0.7 H, *exo*), 2.55−2.65 (m, 0.3 H, *endo*), 2.597 (dd, $J$ = 14.0, 8.4 Hz, 0.7 H, *exo*), 2.66−2.81 (m, 0.7 H, *endo*), 2.772 (dd, $J$ = 14.0, 7.6 Hz, 0.7 H, *exo*), 3.527 (dd, $J$ = 8.8, 4.8 Hz, 0.7 H, *exo*), 3.65 (dd, $J$ = 10.0, 8.4 Hz, 0.3 H, *endo*), 3.90 (t, $J$ = 8.4 Hz, 0.3 H, *endo*), 3.93−3.99 (m, 0.3 H, *endo*), 4.017 (dt, $J$ = 4.8, 4.4 Hz, 0.7 H, *exo*), 4.073 (t, $J$ = s8.4 Hz, 0.7 H, *exo*), 7.14−7.25 (m, 3 H), 7.26−7.32 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 20.4 ($CH_2$, *endo*), 21.1 ($CH_2$, *exo*), 22.1 ($CH_2$, *endo*), 23.6 ($CH_2$, *exo*), 24.5 ($CH_2$, *endo*), 27.4 ($CH_2$, *exo*), 28.3 ($CH_2$, *exo*), 28.6 ($CH_2$, *endo*), 33.5 ($CH_2$, *endo*), 39.7 ($CH_2$, *exo*), 39.9 (CH, *endo*), 42.9 (CH, *exo*), 45.5 (CH, *endo*), 45.6 (CH, *exo*), 70.9 ($CH_2$, *endo*), 71.9 ($CH_2$, *exo*), 76.1 (CH, *exo*), 78.3 (CH, *endo*), 125.9 (CH, *exo*), 126.0 (CH, *endo*), 128.37 (CH, *exo*), 128.40 (CH, *endo*), 128.7 (CH, *exo*), 128.9 (CH, *endo*), 140.6 (C, *exo*), 140.9 (C, *endo*). The stereochemistry of the ring junction was determined by analogy with structurally related 4-substituted 2-oxa-bicyclo[3.4.0]nonane derivatives[38] and NOESY experiments, and the stereochemistry of the 4-position by NOESY experiments as shown below. Cross peaks are observed between $H^1-H^{10}$, $H^{10'}$ and $H^5$−phenyl ortho-protons in the *cis-exo*-isomer and between $H^1-H^4$ in the *cis-trans*-isomer.

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**Supporting Information Available:** Synthesis and reduction of organotellurium, stibine, and bismuthine substrates and NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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