Chalcogen(IV)−Chalcogen(II) Redox Cycles. 1. Halogenation of Organic Substrates with Dihaloselenium(IV) and -tellurium(IV) Derivatives. Dehalogenation of Vicinal Dibromides with Diaryl Tellurides

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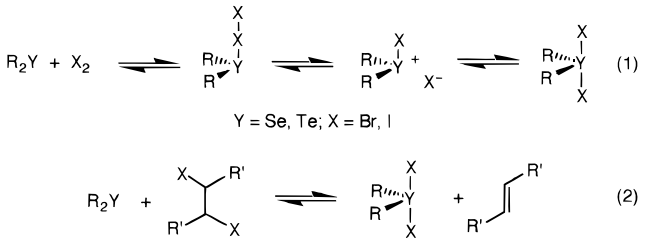
Received June 12, 1996[⊗]

Dibromodiarylselenium(IV) species were efficient sources of positive bromine for bromolactonization of 4-pentenoic acid, bromocyclization of 4-penten-1-ol and 2-buten-1-ol, bromination of 1,3,5-trimethoxybenzene, and bromination of *trans*-stilbene and cyclohexene. These reactions were much slower than brominations with elemental bromine, and product distributions were brominating-agent dependent. Comparable reactions with the diphenylselenide−iodine complex were kinetically indistinguishable from reactions with elemental iodine. Diiododiaryltellurium(IV) species were efficient sources of positive iodine for iodolactonization of 4-pentenoic acid and for the iodocyclization of 4-penten-1-ol. The rates of iodolactonization decreased with increasing electron donation from substituents on the aryl groups. Dibromodiaryltellurium(IV) derivatives gave trace quantities of bromination products in reactions with olefinic substrates. However, diaryl tellurides gave debromination of *erythro*-1,2-dibromo-1,2-diphenylethane to give *trans*-stilbene and the corresponding dibromodiaryltellurium(IV) derivatives. Electron-donating substituents accelerated the rate of debromination. At identical concentrations, debromination of *erythro*-1,2-dibromo-1,2-diphenylethane with diaryl telluride and bromination of *trans*-stilbene with dibromodiaryltellurium(IV) gave identical product mixtures, which is indicative of the equilibrium associated with such halogenation−dehalogenation reactions.

Introduction

Reactions of halogens with diorgano chalcogenides (R_2S, R_2Se, R_2Te) give a variety of bonding arrays at the chalcogen atom including η^1-association complexes, ionic onium species, and formal products of oxidative addition, all of which have been characterized by X-ray crystallography.[1−3] Kinetic and spectroscopic evidence has been described for the sequential generation of these intermediates in oxidative-addition reactions of halogens to diorgano selenides and tellurides as shown in eq 1 of Scheme 1.[2] The oxidative-addition process is reversible,[2,4] and the various equilibria shown in eq 1 are affected by the organic substituents, the chalcogen atoms, and the halogens involved. In principle, the dihalochalcogen(IV) derivatives should function as halogenating species since eq 1 is a reversible process.

Scheme 1



Relatively few examples of halogenation of organic substrates with chalcogen(IV) derivatives have been described. A few examples of chlorination of double and triple bonds with $TeCl_4$ have been described,[5] and the tellurium-catalyzed transfers of halogen from haloethanes to various diynes have also been described.[6] We have recently described diorgano telluride-catalyzed oxidations of halides with hydrogen peroxide to give halogenation of olefinic substrates.[7] Dihalotelluri-

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⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) For η^1-association complexes: (a) McCullough, J. D.; Chao, G. Y.; Zuccaro, D. E. *Acta Crystallogr.* **1959**, *12*, 815. (b) Maddox, H.; McCullough, J. D. *Inorg. Chem.* **1996**, *5*, 522. (c) McCullough, J. D. *Inorg. Chem.* **1964**, *3*, 1425.

(2) For ionic "onium" intermediates: (a) Detty, M. R.; Friedman, A. E.; McMillan, M. *Organometallics* **1994**, *13*, 3338. (b) Detty, M. R.; Friedman, A. E.; McMillan, M. *Organometallics* **1995**, *14*, 1442. (c) Detty, M. R.; Williams, A. J.; Hewitt, J. M.; McMillan, M. *Organometallics* **1995**, *14*, 5258.

(3) For trigonal bipyramidal products of oxidative addition: (a) Chao, G. Y.; McCullough, J. D. *Acta Crystallogr.* **1962**, *15*, 887. (b) McCullough, J. D.; Hamburger, G. *J. Am. Chem. Soc.* **1941**, *63*, 803. (c) Christofferson, G. D.; McCullough, J. D. *Acta Crystallogr.* **1958**, *11*, 249.

(4) McCullough, J. D.; Brunner, A. *Inorg. Chem.* **1967**, *6*, 1251.

(5) (a) Back, T. G. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: Chichester, U.K., 1987; Vol. 2, pp 94−213. (b) Irgolic, K. In *Methods of Organic Chemistry (Houben-Weyl)*, 4th ed.; Klamann, D., Ed.; Thieme Verlag: Stuttgart, Germany, 1990; Vol. E12b. (c) Sudha, N.; Singh, H. B. *Coord. Chem. Rev.* **1994**, *135/136*, 469.

(6) Blum, J.; Baidossi, W.; Badrieh, Y.; Hoffman, R. E.; Schumann, H. *J. Org. Chem.* **1995**, *60*, 4738.

(7) Detty, M. R.; Zhou, F.; Friedman, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 313.

S0276-7333(96)00476-1 CCC: $12.00

um(IV) intermediates were observed and the halogenating agent was either the Te(IV) derivative or a positive halogen source produced by reductive elimination from the Te(IV) derivative. Electrophilic chlorination of the double bonds of dye chromophores from chlorine produced by reductive elimination from Te(IV) has been described and is also an example of this process.[8]

Tellurium reagents have also been used in *dehalogenation* reactions as shown in eq 2 for the reaction of diorgano chalcogenides. The debromination of *vicinal*-dibromoalkanes with diphenyl telluride generates olefins and diphenyltellurium(IV) dibromide.[9] 1,2-Dibromotetrachloroethane has been debrominated by diorgano tellurides to generate dibromotellurium(IV) derivatives.[9,10] In these reactions, the dibromoalkane has been in large excess relative to the diaryl telluride. Inorganic tellurium compounds have also been utilized in dehalogenation reactions including NaHTe and Na_2Te,[11] Te^0 with *O,O*-diethyl phosphite,[12] and bis(triphenylstannyl) telluride.[13]

Of the reagents studied for use in halogenation and dehalogenation reactions, the diorgano chalcogenide derivatives react in both directions in the equilibrium of eq 2. In this manuscript, we describe preliminary studies on this equilibrium. Both halogenation and dehalogenation reactions of organic substrates utilizing diarylchalcogen(IV) and -chalcogen(II) derivatives, respectively, were observed. Factors affecting the equilibrium constant and the absolute rates in the forward and reverse directions include the chalcogen atom and the electronic character of the organic ligands attached to the chalcogen atom.

Results

Iodination Reactions. 4-Pentenoic acid gives iodo lactone **1** upon treatment with either elemental iodine or other sources of positive iodine.[14,15] We examined the iodination of 4-pentenoic acid with various chalcogen(IV) derivatives as comparable sources of positive iodine. Diaryltellurium diiodides **2** were obtained as crystalline solids by the oxidative addition of iodine to diaryl tellurides **3**.[16] The addition of iodine to diphenyl selenide did not give a corresponding crystalline product of oxidative addition. Instead, a dark red oil was produced. The ^{1}H NMR spectrum of the mixture displayed broadened signals at the chemical shifts for the diphenyl selenide multiplets. On the basis of structural studies with other dialkyl selenides and iodine, the diphenyl selenide−iodine product is most likely a mixture of the η^1-association complex of iodine with diphenyl selenide in equilibrium with free diphenyl selenide and iodine.[1]

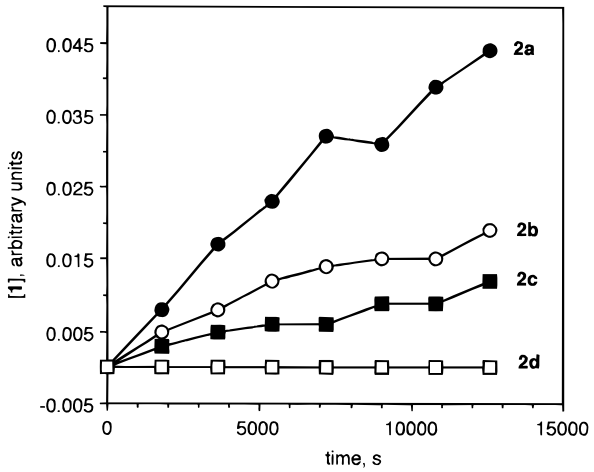
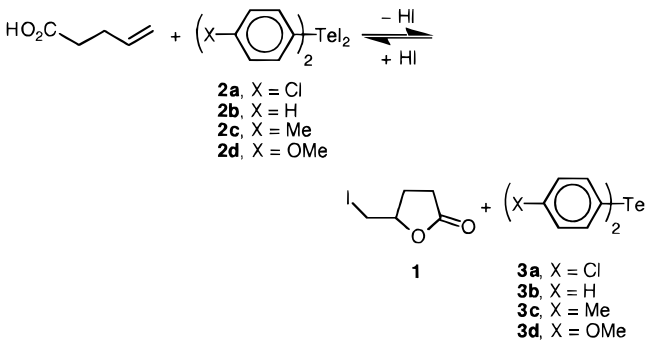


Figure 1. Initial rates of iodolactonization of 4-pentenoic acid (0.01 M) with diiododiaryltellurium(IV) derivatives **2** (0.01 M) in refluxing acetonitrile. The concentrations are in arbitrary units relative to an internal standard of diphenyl ether at 1 mg/mL.

Scheme 2



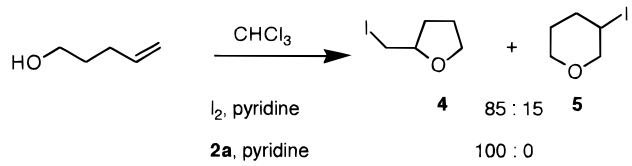
The rates of iodination of 4-pentenoic acid with the various iodination reagents were monitored by gas chromatography (GC). The rate of appearance of **1** was identical for equimolar mixtures of 4-pentenoic acid and either iodine or iodine−diphenyl selenide. Reaction was complete within 1 h at 295 K. In the presence of 1 equiv of added pyridine, the isolated yields of iodo lactone **1** from either iodine or iodine−diphenyl selenide were nearly quantitative (>95%). These data suggest that the diphenyl selenide has little effect on the rate of iodination of 4-pentenoic acid and that the positive iodine reagent is derived from free iodine.

Iodination reactions with diiodotellurium(IV) derivatives **2** were significantly slower than the reaction with free iodine and required several days to reach end points. Within this series, electron-donating substituents in the diaryl telluride slowed the rate of halogenation while electron-withdrawing substituents accelerated the rate of iodination. The initial rates of reactions with diiodotellurium(IV) derivatives **2** are shown in Figure 1.

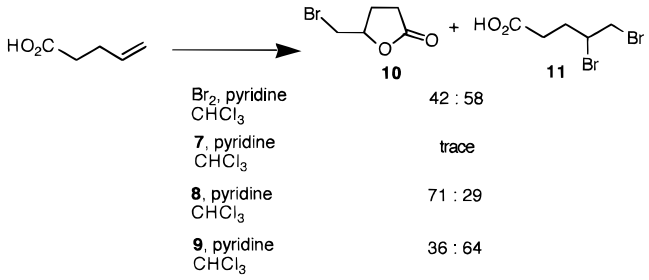
The iodination reactions depicted in Scheme 2 did not go to completion unless the hydroiodic acid was removed. The extent of reaction was a function of concentration of reagents and temperature suggesting that the process of Scheme 2 is reversible. The addition of 1 equiv of pyridine to the reaction mixtures removed the acid from the reaction, which were then driven to completion. Preparative iodination of 4-pentenoic acid with **2a** gave lactone **1** in 65% isolated yield and

(8) Detty, M. R.; Frade, T. M. *Organometallics* **1993**, *12*, 2496.
(9) Campos, M. d. M.; Petragnani, N.; Thomé, C. *Tetrahedron Lett.* **1960**, (15) 5.
(10) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron* **1981**, *37*, Suppl. No. 1, 213.
(11) (a) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574. (b) Barton, D. H. R.; Bohe, L.; Lusinchi, X. *Tetrahedron Lett.* **1987**, *28*, 6609.
(12) Huang, X.; Hou, Yu Q. *Syn. Commun.* **1988**, *18*, 2201.
(13) Li, C. J.; Harpp, D. N. *Tetrahedron Lett.* **1990**, *31*, 6291.
(14) Evans, R. D.; Magee, J. W.; Schauble, J. H. *Synthesis* **1988**, *11*, 862.
(15) Neverov, A. A.; Brown, R. S. *J. Org. Chem.* **1996**, *61*, 962.
(16) (a) The diaryl tellurides were prepared according to: Engman, L.; Persson, J.; Andersson, C. M.; Berglund, M. *J. Chem. Soc. Perkin Trans. 2* **1992**, 1309. (b) The diiodides were prepared according to ref 2b.

Scheme 3



Scheme 4

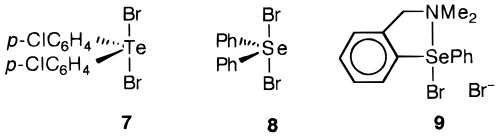


recovered **3a** in 80% isolated yield following chromatographic separation.

Iodocyclization of 4-penten-1-ol with iodine has been reported to give exclusively 2-(iodomethyl)tetrahydrofuran (**4**).[14,15] Under our conditions, iodocyclization of 4-penten-1-ol in $CHCl_3$ with 1 equiv of pyridine at ambient temperature gave an 85:15 mixture of **4** and 2-iodotetrahydropyran (**5**), respectively, as measured by both ^{1}H NMR and GC (Scheme 3). While the reaction with molecular iodine was complete within 1 h, iodocyclization of 4-penten-1-ol with **2a** and 1 equiv of pyridine was complete after 4 days in refluxing chloroform. Compound **4** was isolated from this reaction mixture in 57% yield as the only iodinated product of reaction (Scheme 3). Diaryl telluride **3a** was also recovered in 85% yield.

The diiodotellurium(IV) compounds **2** did not react with 1,3,5-trimethoxybenzene in refluxing $CHCl_3$. After 48 h, both unreacted Te(IV) species and trimethoxybenzene were recovered from the reaction mixtures.

Bromination Reactions. Comparable reactions of chalcogen(IV) derivatives **7**−**9** as sources of positive

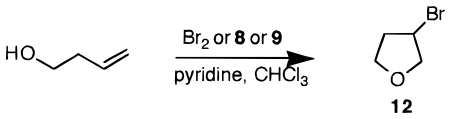


bromine with various olefinic and aromatic substrates were next investigated. Bromination of 4-pentenoic acid has been reported to give bromo lactone **10**.[15,17] Under our conditions, bromination of 4-pentenoic acid gave a 42:58 mixture (^{1}H NMR) of bromo lactone **10** and 4,5-dibromopentanoic acid (**11**), respectively, in $CHCl_3$ with 1 equiv of pyridine (Scheme 4). Halogenation was complete within the time frame of addition. Acid **11** was converted to lactone **10** upon workup with aqueous sodium carbonate.

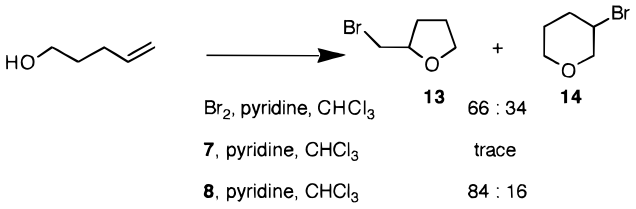
The dibromotellurium(IV) derivative **7** was unreactive toward 4-pentenoic acid and 1 equiv of pyridine in refluxing $CDCl_3$ (Scheme 4). After several days, only trace quantities of bromo lactone **10** were detected by ^{1}H NMR or GC analysis (2−3% conversion). Other more electron-rich dibromotellurium(IV) derivatives (from

(17) Lown, J. W.; Joshua, A. V. *Can. J. Chem.* **1977**, *55*, 508−515.

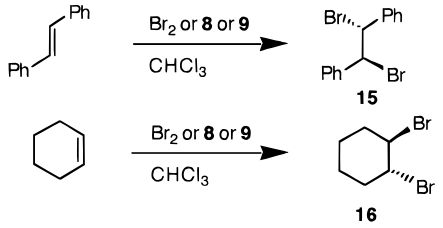
Scheme 5



Scheme 6



Scheme 7



oxidative addition of bromine to **3b**−**d**) gave no detectable amounts of **10**.

The Se(IV) derivatives **8** and **9** gave complete bromination of 4-pentenoic acid at ambient temperature within 1 h. However, the product ratios were quite different for the two reagents. Neutral Se(IV) derivative **8** gave predominantly bromo lactone **10** while ionic Se(IV) derivative **9** gave predominantly the dibromo acid **11** (Scheme 4). Workup with aqueous sodium carbonate gave bromo lactone **10** as well as the diaryl selenide in greater than 85% isolated yields from either mixture.

Bromination of 3-buten-1-ol gives 2-bromotetrahydrofuran (**12**).[15] In $CHCl_3$ at ambient temperature with 1 equiv of pyridine, bromination of 3-buten-1-ol gave **12** as the only product of reaction with bromine (upon mixing), **8** (within 1 h), or **9** (within 1 h) in nearly quantitative yields (Scheme 5). Dibromotellurium(IV) derivative **7** gave traces of **12** after 48 h in refluxing $CDCl_3$ with 1 equiv of pyridine.

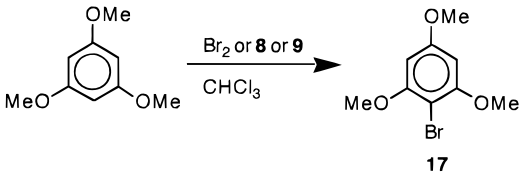
Bromination of 4-penten-1-ol has been reported to give only 2-(bromomethyl)tetrahydrofuran (**13**).[17] Under our conditions, bromination of 4-penten-1-ol in $CHCl_3$ with 1 equiv of pyridine gave a 66:34 mixture (GC and ^{1}H NMR) of **13** and 3-bromotetrahydropyran (**14**), respectively (Scheme 6). Bromination was complete at ambient temperature upon mixing.

Bromination of 4-penten-1-ol with **7** gave traces of **13** after 72 h at reflux in $CDCl_3$ with 1 equiv of pyridine. Bromination with **8** gave an 84:16 mixture (GC and ^{1}H NMR) of **13** to **14**, respectively, after stirring at ambient temperature for 3 h.

The olefinic substrates *trans*-stilbene and cyclohexene were brominated by Se(IV) derivatives **8** and **9** in $CHCl_3$ at ambient temperature as shown in Scheme 7. These reactions were complete within 5 min of addition, and no other products were detected. The Te(IV) derivative **7** gave *erythro*-1,2-dibromo-1,2-diphenylethane (**15**)[18] in

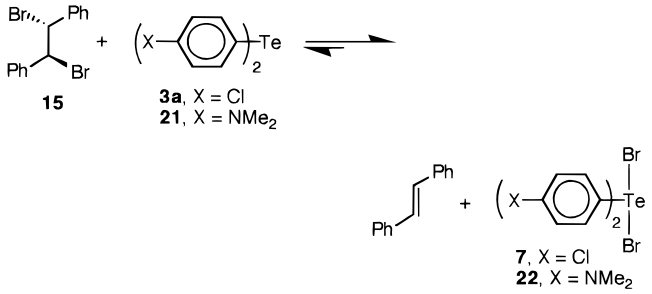
(18) Buckles, R. E.; Bader, J. M.; Thurmaier, R. J. *J. Org. Chem.* **1962**, *27*, 4523−4527.

Scheme 8



17

Scheme 9



15

7, X = Cl
22, X = NMe_2

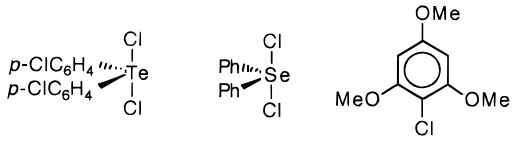
5% yield from *trans*-stilbene and traces of *trans*-1,2-dibromocyclohexane (**16**)[19] from cyclohexene.

Bromination of *trans*-stilbene and cyclohexene on a preparative scale using Se(IV) derivative **8** as the brominating agent gave **15** in 80% isolated yield and **16** in 85% isolated yield, respectively. Diphenyl selenide was recovered in 85% yield from both reactions.

Bromination of 1,3,5-trimethoxybenzene with bromine in $CHCl_3$ gave 1-bromo-2,4,6-trimethoxybenzene (**17**). Varying amounts of 1,3-dibromo-2,4,6-trimethoxybenzene (**18**) (1-15%) were also formed as a function of temperature, reagent concentrations, and rates of addition. The monobromo product **17** is sufficiently reactive toward bromine to give competitive reaction in the mixing regions of bromine addition.

1,3,5-Trimethoxybenzene was also brominated by either **8** or **9** in chloroform at ambient temperature to give **17** in 80% and 92% isolated yields, respectively (Scheme 8) with recovery of the diaryl selenides in >90% yield. When stoichiometric amounts of either **8** or **9** were employed, >99.5% monobromination was observed at ambient temperature. Tellurium(IV) derivative **7** gave only 5% bromination of 1,3,5-trimethoxybenzene after 48 h in refluxing $CHCl_3$.

Chlorination Reactions. Chlorination reactions with **18** and **19** failed to give detectable amounts of



18 **19** **20**

chlorination with cyclohexene, *trans*-stilbene, 4-penten-1-ol, and 4-pentenoic acid. Tellurium(IV) derivative **18** did not chlorinate 1,3,5-trimethoxybenzene. However, Se(IV) derivative **19** gave 1-chloro-2,4,6-trimethoxybenzene (**20**) in quantitative yield within 5 min of mixing at ambient temperature in $CHCl_3$.

Dehalogenation Reactions. If eq 2 of Scheme 1 is correctly written as an equilibrium, then halogenation of an olefin or dehalogenation of a 1,2-dihalide will lead

(19) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469−1476.

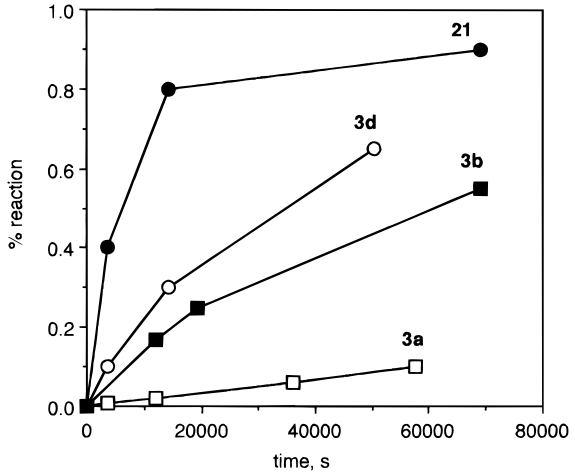


Figure 2. Debromination of *erythro*-1,2-dibromo-1,2-diphenylethane (**15**) with diaryl tellurides **3** and **21** at 368 K. Conversions were determined by ^{1}H NMR integrals of the *trans*-stilbene and *erythro*-1,2-dibromo-1,2-diphenylethane PhC*H*Br− and PhC*H*= singlets.

to the same mixture of products. The reaction of olefinic systems with dibromoselenium(IV) derivatives **8** and **9** gave complete bromination of the olefinic substrates within our detection limits, and not surprisingly, attempted dehalogenation with diphenyl selenide or 2-(*N*,*N*-dimethylaminomethyl)phenyl phenyl selenide gave not a trace of olefinic product. However, bromination of *trans*-stilbene with Te(IV) derivative **7** gave a 19:1 mixture of *trans*-stilbene and *erythro*-1,2-dibromo-1,2-diphenyl ethane (**15**). Debromination of **15** with *p*-chlorophenyl telluride (**3a**), with reagents at the same concentrations as for the bromination reaction, gave a 19:1 mixture of *trans*-stilbene and **15**, respectively. These results suggest that halogenations−dehalogenations with diaryl tellurium derivatives are best represented by the equilibrium shown in Scheme 9. The equilibrium will be a function of the electronic demands of both the olefinic substrates as well as the tellurium-containing reagent.

The initial rates of iodolactonization of 4-pentenoic acid with Te(IV) derivatives **2** as shown in Figure 1 indicate that electron-donating substituents slow the rate of iodine transfer to the olefin. The converse of this statement would suggest that electron-rich tellurides should accelerate dehalogenation reactions of vicinal dihalides. The debromination reactions of **15** with di-*p*-chlorophenyl telluride (**3a**), diphenyl telluride (**3b**), di-*p*-anisyl telluride (**3d**), and di-*p*-(dimethylamino)phenyl telluride (**21**)[16a] were monitored by ^{1}H NMR (Figure 2), and half-lives of 120, 15, 9, and 2 h, respectively, were measured in refluxing chloroform (with identical concentrations of reagents). At completion, the reaction of **15** with **3a** gave a 19:1 mixture of *trans*-stilbene and **15**, respectively, while the reaction of **15** with **21** gave >99% *trans*-stilbene. The more electron-rich diaryl tellurides gave faster debromination in addition to driving the equilibrium of Scheme 9 further to the right.

Preparative debrominations of **15** with **3a** gave *trans*-stilbene in 72% isolated yield. Dibromotellurium(IV) derivative **7** was recovered in 85% isolated yield.

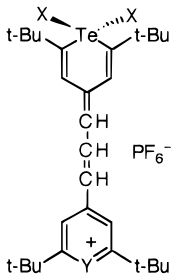
Attempts to debrominate *trans*-1,2-dibromocyclohexane (**16**) were unsuccessful. Trace amounts of cyclohexene were detected by ^{1}H NMR with **3d** and **21** but only in 2−3% conversion. Similar reactions with

erythro-1,2-dichloro-1,2-diphenylethane and *trans*-1,2-dichlorocyclohexane did not even give traces of olefinic products.

Discussion

The bonding array surrounding the dihalodiorganochalcogen(IV) compounds is trigonal bipyramidal with a nearly linear halogen−chalcogen−halogen (X−Y−X) bond angle, distorted from linearity by a lone pair of electrons on the chalcogen atom occupying an equatorial site.[3] The X−Y−X bonding array has been described as either hypervalent or as a delocalized three-center, four-electron bond with both covalent and ionic character.[20] In qualitative terms, the strength of the bond has been defined as a function of the electronegativities of the atoms involved. In particular, strong bonds are formed between electropositive central elements and highly electronegative ligands. The Pauling electronegativities of Se and Te are 2.55 and 2.1, respectively, while the electronegativities of the halogens are 3.16 for Cl, 2.96 for Br, and 2.66 for I.[21] The X−Te−X bonds would be expected to be stronger than the corresponding X−Se−X bonds, with bonds to I being weakest for both chalcogens.

Experimental verification of these predictions has come from reductive elimination and halogen exchange reactions. The bond strengths of Te(IV) dihalides have been measured by the rates of reductive elimination of halogen from Te(IV) dihalides **23** and **24**.[8,22] In these



23, Y = S; X = Br
24, Y = Se, X = Cl

reactions, the Arrhenius energy of activation, E_A, for reductive elimination of bromine from **23** is 4 kcal mol^{-1} lower than E_A for reductive elimination of chlorine from **24**. The rates of tellurium−halogen exchange between diphenyltellurium dihalides and diphenyl telluride suggest that the bond strengths of the Te−X bonds decrease in the following order: Te−F > Te−Cl > Te−Br > Te−I.[23] One would expect similar orderings for Se−X bond strengths although these bonds should be weaker than the corresponding Te−X bonds.

Thermodynamically, the equilibria of eq 1 lie to the right (with the exception, perhaps, of X = I, Y = Se), which is indicative that the chalcogen(IV) dihalide is the thermodynamic sink. However, the rate of halogenation of organic substrates will be a function of the chalcogen−halogen bond strength.

The Se(IV) dibromides are much better brominating agents than the analogous Te(IV) dibromides since the Br−Se−Br bond is weaker than the corresponding Br−Te−Br bond. Even though halogenation−dehalogenation appears to be an equilibrium process, the brominated olefin−diorganoselenium(II) side of the equilibrium is highly favored with organoselenium derivatives being kinetically and thermodynamically better brominating agents than Te(IV) reagents.

Organoselenium compounds do not give extensive (detectable) formation of trigonal-bipyramidal oxidative addition products with iodine, presumably due to the similarities of the electronegativities of Se and I. Tellurium(IV) diiodides with I−Te−I bonds are readily formed, however, and can be used in iodolactonization and other iodocyclization reactions. Electron-withdrawing substituents appear to accelerate the rate of iodine transfer, which is consistent with electron-withdrawing groups decreasing the stability of the Te(IV) oxidation state relative to the Te(II) oxidation state.

Both Se(IV) and Te(IV) dichlorides are unreactive as chlorinating agents for olefinic substrates. The only exception to this observation is the chlorination of 1,3,5-trimethoxybenzene with a Se(IV) dichloride. The electrophilic chlorination of this electron-rich substrate is irreversible once HCl is liberated. The corresponding Te(IV) dichloride was completely unreactive. These observations suggest that the Cl−Se−Cl bond is weaker than the Cl−Te−Cl bond.

The equilibrium shown in Scheme 9 favors the side with the dibromotellurium(IV) derivative and olefin. Electron-donating substituents drive this equilibrium further to the right, which is consistent with electron-donating substituents stabilizing the electron-deficient Te(IV) center more than the more electron-rich Te(II) center.

The product distribution from halogenation of organic substrates is a function of the halogenating agent as illustrated in Scheme 4 for the bromination of 4-pentenoic acid. The differences in product ratios suggest the the positive halogen "carrier" plays a role in the formation of products. If free halogen were the active positive halogen source, one would expect nearly identical product ratios for all reactions. The intermediates of eq 1 of Scheme 1 are all possible positive halogen carriers.

The dehalogenation reactions need not follow the strict reversal of the halogenation pathway. Some possible mechanistic pathways include nucleophilic attack of tellurium at halogen with *trans*-1,2-dehalogenation, concerted *cis*-elimination of the vicinal dihalide with oxidation of the tellurium center, or the formation and fragmentation of telluronium intermediates. We are currently investigating the mechanistic details of both the halogenation and dehalogenation reactions at the chalcogen and carbon centers in order to develop synthetically useful variations of these procedures. In particular, variations of these reactions with chiral diorganochalcogen derivatives may lead to chiral halogenation and dehalogenation reactions.

Experimental Section

General Methods. Solvents (HPLC grade chloroform, dichloromethane, hexanes, ethyl acetate, acetonitrile, acetone),

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cyclohexene, 4-pentenoic acid, 4-pentenol, 3-butenol, 1,3,5-trimethoxybenzene, *trans*-stilbene, pyridine, sodium carbonate, iodine, bromine, and chlorine were used as received from Aldrich Chemical Co. Diphenyl selenide was obtained from Aldrich Chemical Co. and was distilled prior to use. Reactions were stirred magnetically. Concentration *in vacuo* was performed on a Büchi rotary evaporator. Nuclear magnetic resonance spectra were recorded on a Varian Gemini-300 instrument with residual solvent signal as internal standard: $CDCl_3$ (δ 7.26). Infrared spectra were recorded on a Mattson Polaris FT-IR instrument. Gas chromatography was performed on a Shimadzu GC-14A instrument with a 15-m × 0.53-mm ID RTX-5 column (Crossbonded 95% dimethyl−5% diphenyl polysiloxane) from Restek Corp., 110 Benner Circle, Bellefonte, PA. Tellurides **3** and **21** were prepared according to ref 16a.

General Procedure for the Oxidation Addition of Iodine to Diaryl Tellurides. The diaryl telluride **3** (2.0 mmol) was dissolved in 10 mL of acetone. Iodine (0.51 g, 2.0 mmol) was added, and the resulting solution was stirred at ambient temperature for 0.5 h and was then chilled. The crystalline product was collected by filtration, washed with small (2 mL) portions of cold acetone, and dried.

Data for diiodobis(*p*-chlorophenyl)tellurium(IV) (**2a**): Mp 229−231 °C (dec) (lit.[3a] mp 232−233 °C); ^{1}H NMR ($CDCl_3$) δ 8.04 (AA′BB′, 4 H, *J*("doublet") = 9 Hz), 7.40 (AA′BB′, 4 H, *J*("doublet") = 9 Hz).

Data for diiododiphenyltellurium(IV) (**2b**): Mp 232−235 °C (lit.[1b] mp 232−235 °C); ^{1}H NMR ($CDCl_3$) δ 8.14 (m, 4 H), 7.58 (m, 2 H), 7.45 (m, 4 H).

Data for diiodobis(*p*-tolyl)tellurium(IV) (**2c**): Mp 143−145 (dec) (lit.[24] mp 144−147 °C); ^{1}H NMR ($CDCl_3$) δ 7.50 (AA′BB′, 4 H, *J*("doublet") = 9 Hz), 7.35 (AA′BB′, 4 H), 2.27 (s, 6 H).

Data for diiodobis(*p*-anisyl)tellurium(IV) (**2d**): Mp 167−169 °C (lit.[1b] mp 167−169 °C); ^{1}H NMR ($CDCl_3$) δ 8.03 (AA′BB′, 4 H, *J*("doublet") = 9 Hz), AA′BB′, 4 H) 3.87 (s, 6 H).

General Procedure for the Oxidative Addition of Bromine to Diaryl Chalcogenides. The diaryl telluride or selenide (2.0 mmol) was dissolved in 10 mL of acetone. A 2.5-mL aliquot of a 1.0 M solution of bromine in CCl_4 was added dropwise. The resulting solution was stirred 15 min at ambient temperature and was then chilled. The crystalline product was collected by filtration (85−93%), washed with small (2 mL) portions of cold acetone, and dried.

Data for dibromobis(*p*-chlorophenyl)tellurium(IV) (**7**): Mp 182−183 °C; ^{1}H NMR ($CDCl_3$) δ 8.03 (AA′BB′, 4 H, *J*("doublet") = 9 Hz), 7.47 (AA′BB′, 4 H, *J*("doublet") = 9 Hz). Anal. Calcd for $C_{12}H_8Cl_2Br_2Te$: C, 28.33; H, 1.58. Found: C, 28.17; H, 1.67.

Data for dibromodiphenylselenium(IV) (**8**): Mp 149−150 °C dec with gas evolution (lit.[1a] mp 149−150 °C dec); ^{1}H NMR ($CDCl_3$) δ 8.04 (br d, 4 H), 7.60−7.45 (m, 6 H).

General Procedure for the Oxidative Addition of Chlorine to Diaryl Chalcogenides. The diayl telluride or selenide (2.0 mmol) was dissolved in 2.5 mL of $CHCl_3$. A 2.5-mL aliquot of a 1.0 M solution of chlorine in CCl_4 was added dropwise. The resulting solution was stirred 15 min at ambient temperature and was then chilled. The crystalline product was collected by filtration (55−75%), washed with small (2 mL) portions of cold $CHCl_3$, and dried.

Data for dichlorobis(*p*-chlorophenyl)tellurium(IV) (**18**): Mp 187−193 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.13 (AA′BB′, 4 H, *J*("doublet") = 9 Hz), 7.47 (AA′BB′, 4 H, *J*("doublet") = 9 Hz). Anal. Calcd for $C_{12}H_8Cl_4Te$: C, 34.18; H, 1.92. Found: C, 33.88; H, 1.77.

Data for dichlorodiphenylselenium(IV) (**19**): Mp 173 °C dec with gas evolution; ^{1}H NMR ($CDCl_3$) δ 8.14 (br d, 4 H), 7.60−7.45 (m, 6 H).

Preparation of Bromo(2-(*N*,*N*-Dimethylaminomethyl)-phenyl)phenylselenonium(IV) Bromide (9). To a solution of dimethylbenzylamine (1.35 g, 0.0100 mol) in 50 mL of ether at −78 °C was added 10.5 mL of 1.0 M *tert*-BuLi in hexanes (0.0105 mol). The resulting solution was warmed to ambient temperature and stirred for 3 h. A solution of phenylselenyl chloride (1.91 g, 0.0100 mol) in 20 mL of THF was added dropwise. The reaction mixture was poured into water, and the organic phase was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified via chromatography on silica gel eluted with dichloromethane to give 0.97 g (33%) of 2-(*N*,*N*-dimethylaminomethyl)phenyl phenyl selenide as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.53 (m, 2 H), 7.3 (m, 5 H), 7.15 (m, 2 H), 7.05 (m, 1 H) 3.52 (s, 2 H), 2.24 (s, 6 H); FDMS *m*/*z* 291 ($C_{15}H_{17}N^{80}Se$).

To a solution of 2-(*N*,*N*-dimethylaminomethyl)phenyl phenyl selenide (0.87 g, 3.0 mmol) in 20 mL of acetone was added bromine (0.48 g, 3.0 mmol). The resulting solution was stirred until bright yellow crystals of **9** began to precipitate. The reaction mixture was chilled, and the crystals were collected by filtration to give 1.21 g (90%) of **8**, mp 183−187 °C (dec with gas evolution). Anal. Calcd for $C_{15}H_{17}Br_2NSe$: C, 40.03; H, 4.03; N, 3.11. Found: C, 39.87; H, 4.13; N, 3.23.

Iodination of 4-Pentenoic Acid with Iodine. 2-Oxo-4-(iodomethyl)tetrahydrofuran (**1**) was prepared by the addition of iodine (0.254 g, 1.00 mmol) to a dichloromethane solution of 4-pentenoic acid (0.100 g, 1.00 mmol) containing 1.25 equiv (0.100 g) of pyridine. The reaction mixture was washed with water, 5% HCl, saturated $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated. The residue was purified via chromatography on silica gel eluted with CH_2Cl_2 to give 0.21 g (60%) of **1**[4,15] as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 4.52 (m, 1 H), 3.39 (ABX, 1 H), 3.27 (ABX, 1 H), 2.35−2.7 (m, 3 H), 1.96 (m, 1 H); IR (film, NaCl) 1776 cm^{-1}; FDMS *m*/*z* 226.5 ($C_5H_7O_2I$).

Iodination of 4-Pentenoic Acid with Diiodobis(*p*-chlorophenyl)tellurium(IV) (2a). A solution of 4-pentenoic acid (0.0500 g, 0.500 mmol), **2a** (0.302 g, 0.500 mmol), and pyridine (0.040 g, 0.500 mmol) was heated at reflux in 20 mL of chloroform for 5 days. The reaction mixture was concentrated *in vacuo*, and the residue was purified via chromatography on silica gel eluted with 1:1 hexanes−ethyl acetate to give 0.073 g (66 %) of **1** and 0.140 mg (80 %) of **3a**.

General Proceudre for Kinetic Comparisons of the Iodination of 4-Pentenoic Acid with Diiododiaryltellurium(IV) Derivatives. A solution of 4-pentenoic acid (0.0100 g, 0.100 mmol) and diiododiaryltellurium(IV) derivative (0.100 mmol) was dissolved in 10.0 mL of acetonitrile. Diphenyl ether (0.0100 g) was added as an internal standard. The resulting solutions were stirred in a 95 °C oil bath. The reaction mixtures were sampled periodically by GC (injector, 200 °C; column, 60 °C; detector, 250 °C), and the conversions to product **1** in arbitrary units were compared relative to the internal standard.

Iodination of 4-Penten-1-ol with Iodine. An 85:15 mixture of 4-(iodomethyl)tetrahydrofuran (**4**) and 3-iodotetrahydropyran (**5**) was prepared by the addition of iodine (0.254 g, 1.00 mmol) to a dichloromethane solution of 4-penten-1-ol (0.086 g, 1.00 mmol) containing 1.25 equiv (0.100 g) of pyridine. The reaction mixture was washed with water, 5% HCl, saturated $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated. The residue was purified via chromatography on silica gel eluted with CH_2Cl_2 to give 0.24 g (70%) of the mixture of **4**[14,15] and **5**[14,15] as a colorless oil. Data for 4-(iodomethyl)-tetrahydrofuran (**4**): ^{1}H NMR ($CDCl_3$) δ 3.95 (m, 2 H), 3.81 (m, 1 H), 3.24 (dxd, 1 H, *J* = 5.2, 9.9 Hz), 3.18 (dxd, 1 H, *J* = 6.6, 9.9 Hz), 2.10 (m, 1 H), 1.95 (m, 2 H), 1.65 (m, 1 H); FDMS *m*/*z* 212.5 (C_5H_9OI) for the mixture.

Data for 3-iodotetrahydropyran (**5**): ^{1}H NMR ($CDCl_3$) δ 4.35 (m, 2 H), 4.11 (t, 1 H, *J* = 14 Hz), 4.04 (m, 2 H), 2.23 (m, 1 H), 1.85 (m, 2 H), 1.65 (m, 1 H).

Iodination of 4-Penten-1-ol with Diiodobis(*p*-chlorophenyl)tellurium(IV) (2a). A solution of 4-pentenol (0.0860 g, 1.00 mmol), **2a** (0.605 g, 1.00 mmol), and pyridine (0.080 g,

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1.00 mmol) was heated at reflux in 10 mL of chloroform for 4 days. The reaction mixture was concentrated *in vacuo*, and the residue was purified via chromatography on silica gel eluted with 1:1 hexanes−ethyl acetate to give 0.121 g (57%) of **4** and 0.30 g (85%) of **3a**. The ^{1}H NMR spectrum of the crude reaction mixture showed only a mixture of pyridinium iodide, **4**, and telluride **3a**.

Bromination of 4-Pentenoic Acid with Bromine. 2-Oxo-4-(bromomethyl)tetrahydrofuran (**10**) was prepared by addition of bromine (0.160 g, 1.00 mmol) to a dichloromethane solution of 4-pentenoic acid (0.100 g, 1.00 mmol) containing 1.25 equiv (0.100 g) of pyridine. The crude reaction mixture was washed with water, dried over $MgSO_4$, and concentrated to give a 42:58 mixture of 2-oxo-4-(bromomethyl)tetrahydrofuran (**10**) and 4,5-dibromopentanoic acid (**11**), respectively.

Data for 2-oxo-4-(bromomethyl)tetrohydrofuran (**10**):[15,17] ^{1}H NMR ($CDCl_3$) δ 4.69 (m, 1 H), 3.51 (m, 2 H), 2.7−2.4 (m, 2 H), 2.38 (m, 1 H), 2.08 (m, 1 H); IR (film, NaCl) 1780 cm^{-1}; *m*/*z* 180 ($C_5H_7{}^{81}BrO_2$).

Data for 4,5-dibromopentanoic acid (**11**): ^{1}H NMR ($CDCl_3$) δ 4.21 (m, 1 H), 3.85 (d × d, 1 H, J = 4, 10 Hz), 3.61 (d × d, 1 H, J = 9, 10 Hz), 2.45−2.7 (m, 3 H), 2.03 (m, 1 H); IR (film, NaCl) 3050 (br), 1711 cm^{-1}; FDMS *m*/*z* 262 ($C_5H_8{}^{81}Br_2O_2$).

The reaction mixture was washed with 10% Na_2CO_3 and brine, dried over $MgSO_4$, and concentrated. The residue was purified via chromatography on silica gel eluted with CH_2Cl_2 to give 0.16 g (60%) of **10**[14,15] as a colorless oil, free from **11**.

General Procedure for Bromination of Organic Substrates. Bromination of 4-Pentenoic Acid with Dibromodiphenylselenium(IV) (8). A solution of 4-pentenoic acid (0.100 g, 1.00 mmol), **8** (0.393 g, 1.00 mmol), and pyridine (0.080 g, 1.00 mmol) in 5 mL of CH_2Cl_2 was stirred for 10 min at ambient temperature. The reaction mixture was concentrated *in vacuo*, and the residue was examined by ^{1}H NMR and by mass spectroscopy. Diphenyl selenide, **10**, and 4,5-dibromopentanoic acid (**11**) were the only observed products (71:29 ratio of **10**:**11** by ^{1}H NMR). The crude reaction mixture was redissolved in dichloromethane, washed with 10% Na_2CO_3 solution, dried over purified $MgSO_4$, and concentrated. Purification via chromatography on silica gel eluted with 1:1 hexanes−ethyl acetate gave 0.161 g (90%) of **10** and 0.189 mg (85%) of diphenyl selenide.

Bromination of 4-Pentenoic Acid with Dibromobis(*p*-chlorophenyl)tellurium(IV) (7). A solution of **7** (51 mg, 0.10 mmol), pyridine-d_5 (8.3 mg, 0.10 mmol), and 4-pentenoic acid (10.0 mg, 0.10 mmol) in 3 mL of $CDCl_3$ was heated in a 95 °C oil bath. The reaction mixture was sampled periodically by ^{1}H NMR and GC and showed only trace amounts of **10** after 72 h.

Bromination of 4-Pentenoic Acid with Bromo(2-(*N*,*N*-dimethylaminomethyl)phenyl)phenylselenonium(IV) Bromide (9). A solution of 4-pentenoic acid (0.100 g, 1.00 mmol), **9** (0.450 g, 1.00 mmol), and pyridine (0.080 g, 1.00 mmol) was treated as described above. The reaction mixture was concentrated *in vacuo*, and the residue was examined by ^{1}H NMR revealing a 36:64 ratio of **10**:**11**. The crude reaction mixture was redissolved in dichloromethane, washed with Na_2CO_3 solution, dried over purified $MgSO_4$, and concentrated. Purification via chromatography on silica gel eluted with 1:1 hexanes−ethyl acetate gave 0.153 g (85%) of **10** and 0.204 mg (88%) of 2-(*N*,*N*-dimethylaminomethyl)phenyl phenyl selenide.

Bromination of 3-Buten-1-ol with 8 or 9. A solution of 3-buten-1-ol (0.072 g, 1.00 mmol), **8** or **9** (1.00 mmol), and pyridine (0.080 g, 1.00 mmol) was treated as described above. The reaction mixture was concentrated *in vacuo*, and the residue was examined by ^{1}H NMR revealing diaryl selenide and 3-bromotetrahydrofuran (**12**) as the only products.

Data for 3-bromotetrahydrofuran (**12**):[15] ^{1}H NMR ($CDCl_3$) δ 4.38 (m, 1 H), 3.83 (m, 3 H), 3.66 (d × d, 1 H, J = 12, 15 Hz), 2.40 (m, 1 H), 1.91 (m, 1 H); FDMS *m*/*z* 152 ($C_4H_7{}^{81}BrO$).

Bromination of 3-Buten-1-ol with Dibromobis(*p*-chlorophenyl)tellurium(IV) (7). A solution of **7** (51 mg, 0.10 mmol), pyridine-d_5 (8.3 mg, 0.10 mmol), and 3-buten-1-ol (7.2 mg, 0.10 mmol) in 3 mL of $CDCl_3$ was heated in a 95 °C oil bath. The reaction mixture was sampled periodically by ^{1}H NMR and showed only trace amounts of **12** after 48 h.

Bromination of 4-Penten-1-ol with 8. A solution of 4-penten-1-ol (0.086 g, 1.00 mmol), **8** (0.393 g, 1.00 mmol), and pyridine (0.080 g, 1.00 mmol) was treated as described above. The reaction mixture was concentrated *in vacuo*, and the residue was examined by ^{1}H NMR revealing an 84:16 ratio of **13**:**14** in addition to diphenyl selenide. The products were not separated. Mass spectral analysis indicated a large *m*/*z* 166 peak, which is consistent with either product ($C_5H_9{}^{81}BrO$) as well as the expected isotope cluster for diphenyl selenide *m*/*z* 234 ($C_{12}H_{10}{}^{80}Se$).

Data for 2-(bromomethyl)tetrahydrofuran (**13**:[17] ^{1}H NMR ($CDCl_3$) δ 4.11 (m, 1 H), 3.88 (m, 1 H), 3.79 (m, 1 H), 3.35 (ABX, 2 H), 2.05 (m, 1 H), 1.90 (m, 1 H), 1.7 (m, 1 H).

Data for 3-bromotetrahydropyran (**14**):[17] ^{1}H NMR ($CDCl_3$) δ 4.18 (m, 1 H), 3.75 (m, 1 H), 3.7−3.55 (m, 3 H), 2.23 (m, 1 H), 1.85 (m, 2 H), 1.65 (m, 1 H).

Bromination of 4-Penten-1-ol with Dibromobis(*p*-chlorophenyl)tellurium(IV) (7). A solution of **7** (51 mg, 0.10 mmol), pyridine-d_5 (8.3 mg, 0.10 mmol), and 4-penten-1-ol (8.6 mg, 0.10 mmol) in 3 mL of $CDCl_3$ was heated in a 95 °C oil bath. The reaction mixture was sampled periodically by ^{1}H NMR and showed only trace amounts of **13** after 72 h.

Bromination of *trans*-Stilbene with 8. A solution of *trans*-stilbene (0.36 g, 2.0 mmol) and **8** or **9** (0.98 g, 2.5 mmol) in 7 mL of $CHCl_3$ was heated to reflux and then chilled. The crystalline **15** was collected by filtration and washed with cold $CHCl_3$ to give 0.541 g (80%) of **15**.

Data for *erythro*-1,2-dibromo-1,2-diphenylethane (**15**): Mp 236−237 °C (lit.[18] mp 237−238 °C); ^{1}H NMR ($CDCl_3$) δ 7.50 (AA′BB′, 4 H), 7.37 (m, 6 H), 5.46 (s, 2 H); FDMS *m*/*z* 342 ($C_{14}H_{12}{}^{81}Br_2$).

Bromination of Cyclohexene with 8. A solution of cyclohexene (0.329 g, 4.0 mmol) and **8** (1.57 g, 4.00 mmol) in 10 mL of CH_2Cl_2 was stirred for 5 min. The reaction mixture was concentrated, and the products were separated by chromatography on silica gel eluted with 5% ethyl acetate−hexane to give 0.823 g (85%) of **16** and 0.84 g (90%) of diphenyl selenide.

Data for *trans*-1,2-dibromocyclohexane (**16**):[19] ^{1}H NMR ($CDCl_3$) δ 4.41 (m, 2 H), 2.42 (m, 2 H), 1.83 (m, 4 H), 1.50 (m, 2 H); FDMS *m*/*z* 244 ($C_6H_{10}{}^{81}Br_2$).

Bromination of 1,3,5-Trimethoxybenzene with 8 or 9. A solution of **8** or **9** (3.00 mmol) in 15 mL of CH_2Cl_2 was added dropwise to a stirred solution of 1,3,5-trimethoxybenzene (0.505 g, 3.00 mmol) and sodium carbonate (0.636 g, 6.00 mmol) in 15 mL of CH_2Cl_2. The reaction mixture was quenched with water, and the organic phase was dried over magnesium sulfate and concentrated. The crude product mixture was dissolved in 10 mL of hexanes and chilled. The bromo-2,4,6-trimethoxybenzene was collected by filtration, washed with small portions of cold hexanes, and dried to give 0.593 g (80%) of **17** from **8** and 0.681 g (92%) of **17** from **9**. The diaryl selenides were recovered from the mother liquors in >90% yields.

Data for 2-bromo-1,3,5-trimethoxybenzene (**17**): Mp 91−93 °C; ^{1}H NMR ($CDCl_3$) δ 6.16 (s, 2 H), 3.86 (s, 6 H), 3.80 (s, 3 H); FDMS *m*/*z* 232 ($C_9H_{11}{}^{81}BrO_2$).

Chlorination of 1,3,5-Trimethoxybenzene with 19. A solution of **19** (0.304 g, 1.00 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a stirred solution of 1,3,5-trimethoxybenzene (0.168 g, 1.00 mmol) and pyridine (0.080 g, 1.00 mmol) in 5 mL of CH_2Cl_2. The reaction mixture was quenched with water, and the organic phase was dried over magnesium sulfate and concentrated. The crude product mixture was dissolved in 5 mL of hexanes and chilled. The chloro-2,4,6-trimethoxybenzene was collected by filtration, washed with small portions of cold hexanes, and dried to give 0.235 g (99%)

of **20**. The diphenyl selenide was recovered from the mother liquors in >90% yield.

Data for 2-chloro-1,3,5-trimethoxybenzene (**20**): Mp 72−74 °C; ^{1}H NMR ($CDCl_3$) δ 6.14 (s, 2 H), 3.82 (s, 6 H), 3.78 (s, 3 H); FDMS *m*/*z* 186 ($C_9H_{11}{}^{35}ClO_2$).

Bromination of *trans*-Stilbene with Dibromobis(*p*-chlorophenyl)tellurium(IV) (7). A solution of **7** (51 mg, 2.63 mmol) and *trans*-stilbene (1.34 g, 2.63 mmol) in 20 mL of $CHCl_3$ was heated at reflux for 5 days. The ^{1}H NMR spectrum of the reaction mixture showed a 19:1 mixture of *trans*-stilbene to **15**.

Debromination of *erythro*-1,2-Dibromo-1,2,-diphenylethane (15) with Tellurides 3a,b,d and 21. Solutions of diaryl telluride (0.010 mmol; 3.5 mg for **3a**, 2.8 mg for **3b**, 3.4 mg for **3d**, and 3.7 mg for **21**) and *erythro*-1,2-dibromo-1,2-diphenylethane (**15**, 3.4 mg, 0.010 mmol) in 1.0 mL of $CDCl_3$ were prepared in 5-mm NMR tubes, sealed, and immersed in a 95 °C oil bath. The ^{1}H NMR spectra of the reaction mixtures were recorded periodically and the ratio of the PhC*H*Br− and PhC*H*= singlets determined by integration.

Preparative-Scale Debromination of *erythro*-1,2-Dibromo-1,2,-diphenylethane (15) with Tellurides 3a and 21. A solution of bis(*p*-chlorophenyl)telluride (0.921 g, 2.63 mmol) and *erythro*-1,2-dibromo-1,2-diphenylethane (**15**, 0.893 g, 2.63 mmol) in 20 mL of $CHCl_3$ was heated at reflux for 15 days. The ^{1}H NMR spectrum of the reaction mixture at this time displayed a 19:1 mixture of *trans*-stilbene to **15**. The reaction mixture was chilled precipitating the dibromide **7**, which was collected by filtration (1.07 g, 85%). The residue was purified via chromatography on silica gel eluted with hexanes to give *trans*-stilbene in 72% isolated yield.

A similar reaction with bis(*p*-*N*,*N*-dimethylanilino) telluride (**21**) gave complete conversion to *trans*-stilbene and dibromide **22** in 18 h. By ^{1}H NMR, <1% *erythro*-1,2-dibromo-1,2-diphenylethane (**15**) remained.

Acknowledgment. The authors acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

OM960476K