Debrominations of *vic*-Dibromides with Diorganotellurides. 1. Stereoselectivity, Relative Rates, and Mechanistic Implications

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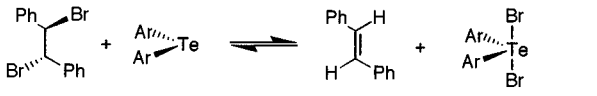
Debrominations of *vic*-dibromides with diaryl tellurides **1**−**4** and di-*n*-hexyl telluride (**9**) are described. A mechanistic explanation of the debromination is offered which accounts for several key experimental observations: (1) the reaction is highly stereoselective with *erythro*-dibromides giving *trans*-olefins and *threo*-dibromides giving *cis*-olefins, (2) the reaction is accelerated by more electron-rich diorganotellurides, (3) the reaction is accelerated in a more polar solvent, (4) the reaction is accelerated by the addition of carbocation-stabilizing substituents to the carbons bearing the bromo substituents, and (5) *erythro*-dibromides are much more reactive than *threo*-dibromides. It is proposed that bromonium ion formation from the *vic*-dibromide is slow and rate-determining. Bromonium ion formation is followed by rapid scavenging of "Br^+" by the diorganotelluride. The bromonium ion formation provides stereoselectivity and eclipsing interactions lower the reactivity of *threo*-dibromides. No intermediate species were observed by ^{1}H NMR.

Bromination of olefins is one of the first general reactions that students of organic chemistry study.[1] The reaction is characterized by stereospecific *anti*-addition to the double bond in most substrates. The stereospecificity is a consequence of a bromonium ion intermediate,[2] which is opened by back-side attack of bromide. The olefins can be regenerated from these *vic*-dibromides with a variety of reagents,[3] and the overall bromination/debromination process represents a means of protection/deprotection of olefins. Stereospecificity in the dehalogenation step is a critical issue in this chemistry.

In 1960, Campos, Petragnani, and Thomé reported the debromination of *vic* dibromides with diaryl tellurides to give olefins and diaryltellurium(IV) dibromides.[4] One intriguing observation in this report was the isolation of ethano-bridged bis(diphenyltelluronium) salts from the reaction of 1,2-dibromoethane with diphenyl telluride, which suggested that telluronium salts might be intermediates in the debromination process. Other studies have shown that debromination reactions of *erythro*-1,2-dibromo-1,2-diphenylethane with diaryl tellurides are equilibria as shown in eq 1.[5] Organoselenium(IV) derivatives are useful as halogenating agents for olefinic substrates since similar reactions with organoselenium compounds are equilibria which lie far to the left.[5]



(1)

1, Ar = *p*-$Me_2NC_6H_4$
2, Ar = *p*-$MeOC_6H_4$
3, Ar = Ph
4, Ar = *p*-ClC_6H_4

5, Ar = *p*-$Me_2NC_6H_4$
6, Ar = *p*-$MeOC_6H_4$
7, Ar = Ph
8, Ar = *p*-ClC_6H_4

If chalcogen−carbon bond formation were involved in bromination/debromination, one might envision chiral halogenating agents as well as enantioselective dehalogenating agents based on this chemistry.[6] Brominations with Se(IV) derivatives and debrominations with Te(II) derivatives may involve similar intermediates. Little is known about the mechanisms associated with dehalogenation of vicinal dibromides with organotellurides or with halogenation with Se(IV) dihalides or the factors which influence the equilibria shown in eq 1.[4,5] In this paper, the mechanism of debromination of *vic*-dibromides with diorganotellurides is explored. Stereoselectivity in olefin formation from *vic*-dibromides of known geometry was chosen as a probe of the mechanism of reaction as were

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(1) (a) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, 1973; pp 186−187. (b) Streitweiser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillan: New York, 1981; pp 307−311. (c) Vollhardt, K. P. C.; Shore, N. E. *Organic Chemistry*, 2nd ed.; W. H. Freeman: New York, 1994; pp 423−425. (d) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry. Part B: Reactions and Synthesis*, 3rd ed.; Plenum Press: New York, 1990; pp 176−177.

(2) (a) Olah, G. A.; Bollinger, J. M.; Brinich, J. *J. Am. Chem. Soc.* **1968**, *90*, 2587−2594. (b) Olah, G. A., Schilling, P.; Westerman, P. W.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581−3589. (c) Strating, J.; Wierenga, J. H.; Wyberg, H. *J. Chem. Soc., Chem. Commun.* **1968**, 907−908. (d) Olah, G. *Halonium Ions*; Wiley: New York, 1975; Chapter 7.

(3) With I^-: (a) Plattner, P. A.; Heusser, H.; Segre, *Helv. Chim. Acta* **1948**, *31*, 249−255. (b) Solo, A. J.; Singh, B. *J. Org. Chem.* **1965**, *30*, 1658−1659. With Zn and Mg: (c) Baciocchi, E. In *Chemistry of Functional Groups, Supplement D, Part 1*; Patai, S., Rappoport, H., Eds.; Wiley: New York, 1983. With Te reagents: (d) Campos, M. M.; Petragnani, N. *Chem. Ber.* **1961**, *94*, 1759−1766. (e) Ramasamy, K.; Kalyanasundarani, S. K.; Shammugan, P. *Synthesis* **1978**, 311−312. (f) Engman, L. *Tetrahedron Lett.* **1982**, *23*, 3601−3602. (g) Suzuki, H.; Inouye, M. *Chem. Lett.* **1985**, 225−228. (h) Huang, X.; Hou, Yu Q. *Synth. Commun.* **1988**, *18*, 2201−2204. (i) Li, C. J.; Harpp, D. N. *Tetrahedron Lett.* **1990**, *31*, 6291−6294. (j) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574−1578. (k) Barton, D. H. R.; Bohe, L.; Lusinchi, X. *Tetrahedron Lett.* **1987**, *28*, 6609−6612. (l) Desilva, K. G. K.; Monsef-Mirzai, Z.; McWhinnie, W. R. *J. Chem. Soc., Dalton Trans.* **1983**, 2143-2146.

(4) Campos, M. d. M.; Petragnani, N.; Thomé, C. *Tetrahedron Lett.* **1960**, (15) 5−8.

(5) Leonard, K. A.; Zhou, F.; Detty, M. R. *Organometallics* **1996**, *15*, 4285−4292.

(6) Examples of chiral face selectivity have been reported with organoselenium reagents: (a) Fujita, K.; Iwaoka, M.; Tamoda, S. *Chem. Lett.* **1994**, 923−926. (b) Wirth, T. *Tetrahedron Lett.* **1995**, *36*, 7849−7852. (c) Wirth, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1726−1728.

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the effects of diorganotelluride structure, dibromide structure, solvent polarity, and reagent concentrations.

Results and Discussion

A. Electronic Effects at Tellurium. In debromination reactions of *erythro*-1,2-dibromo-1,2-diphenylethane in refluxing $CDCl_3$ (eq 1), electron-rich diaryl tellurides give faster debromination than more electron-deficient diaryl tellurides with $(p\text{-}Me_2NC_6H_4)_2Te$ (**1**[7]) > $(p\text{-}MeOC_6H_4)_2Te$ (**2**[7]) > Ph_2Te (**3**) > $(p\text{-}ClC_6H_4)_2Te$ (**4**[7]).[5] In these stoichiometric reactions, values of K_{eq} were between 80 and 170 with K_{eq} (as a function of telluride structure) decreasing in the following order: **1** > **2** > **3** > **4**. The olefinic product in this dehalogenation reaction is *trans*-stilbene (formed with ≥ 98% stereoselectivity), and the Te(IV) derivative is the corresponding diaryltellurium dibromide (**5**−**8**, respectively). Electron-rich diaryl tellurides appear to drive the equilibrium to the right as well as to accelerate the rate of dehalogenation.

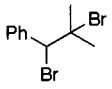
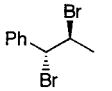
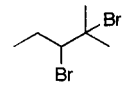
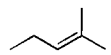
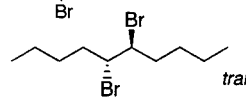
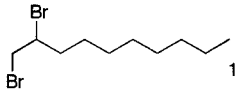
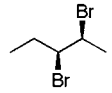
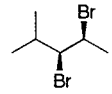
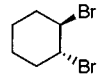
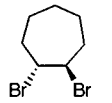
The tellurium atom of dialkyl tellurides is more nucleophilic than the tellurium atom of diaryl tellurides.[8,9] Di-*n*-hexyl telluride (**9**) is conveniently prepared in 56% isolated yield from disodium telluride and 1-bromohexane. In stoichiometric reactions of **9** (0.10 M) with *erythro*-1,2-dibromo-1,2-diphenylethane (0.10 M) in $CDCl_3$, >98% conversion to *trans*-stilbene and dihexyltellurium(IV) dibromide (**10**) was observed after 30 h ($K_{eq} \geq 2500$) in refluxing $CDCl_3$.

In the debromination of *erythro*-1,2-dibromo-1,2-diphenylethane, the stilbene product is highly conjugated. It is not surprising that values of K_{eq} are significantly smaller in examples where added conjugation is not a driving force for dehalogenation.

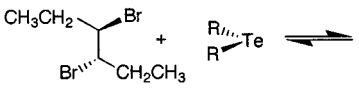
Debromination of *erythro*-3,4-dibromohexane (0.10 M) with **1** (0.10 M) gave only 25% conversion in $CDCl_3$ (at 100 °C) to *trans*-3-hexene (no *cis*-3-hexene was detected by ^1H NMR with a detection limit of ≤ 2%) and **5** after 61 h (eq 2). Equimolar mixtures (0.10 M) of *trans*-hexene and **5** slowly gave *erythro*-3,4-dibromohexane and **1** (≈25% conversion after 240 h at 100 °C). Although equilibrium was not reached, the upper limit for K_{eq} is 9 under these conditions. Diphenyl telluride (**3**) was kinetically poor in promoting debromination of *erythro*-3,4-dibromohexane with less than 10% conversion to *trans*-3-hexene after 240 h in $CDCl_3$ at 100 °C. The more electron-deficient telluride **4** showed no detectable olefinic product from *erythro*-3,4-dibromohexane after 240 h in $CDCl_3$ at 100 °C. Di-*n*-hexyl telluride **9** (0.10 M) gave 65% conversion of *erythro*-3,4-dibromohexane (0.10 M) to *trans*-3-hexene and **10** after 61 h in $CDCl_3$ at 100 °C.

B. Dibromide Structure. The debromination of *vic*-dibromides with di-*n*-hexyl telluride (**9**) was a general reaction for the substrates shown in Table 1 (0.10 M in both reagents). In reactions of all of the substrates of Table 1 with telluride **9**, no intermediate species were observed. As the reactions progressed, ^1H and ^{13}C NMR signals were detected for the telluride **9**, Te(IV) derivative **10**, *vic*-dibromide, and olefin. Control reactions showed that the acyclic *vic*-dibromides were thermally stable to the conditions of reaction. However, *trans*-1,2-dibromocyclohexane and *trans*-1,2-dibromocycloheptane slowly gave cyclohexene and cycloheptene, respectively, via a thermal process (≈10% conversion after 300 h at 100 °C).

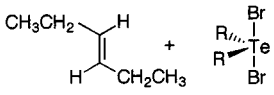
Table 1. Dibromides, Their Olefinic Products, and Relative Rates of Debromination of *vic*-Dibromides with Dihexyl Telluride (9) in $CDCl_3$ and CD_3CN at (90 ± 1) °C

entry	dibromide	olefin[a]	k_{rel} ($CDCl_3$)	k_{rel} (CD_3CN)
(1)			330	222
(2)			305	--
(3)			104	95
(4)		*trans*-5-decene	2	2.7
(5)		1-decene	1	1
(6)			≤ 0.05	≤ 0.05
(7)			≤ 0.05	≤ 0.05
(8)			≤ 0.05	≤ 0.05
(9)			2	--

[a] Products were ≥ 98% stereochemically pure as determined by ^1H and ^{13}C NMR spectroscopy.



1, R = p-$Me_2NC_6H_4$
9, R = n-C_6H_{13}



(2)

5, R = p-$Me_2NC_6H_4$
10, R = n-C_6H_{13}

Precursors to trisubstituted olefins gave excellent conversions to the olefinic products. Debromination of 1,2-dibromo-2-methyl-1-phenylpropane (entry 1, Table 1) with **9** gave >98% conversion in $CDCl_3$ to 2-methyl-1-phenylpropene and Te(IV) dibromide **10** after 24 h at 100 °C. Debromination of 2,3-dibromo-2-methylpentane was somewhat slower, giving 95% conversion to 2-methyl-2-pentene after 72 h at 100 °C in $CDCl_3$ (entry 3, Table 1).

Debromination of *erythro*- and *threo*-dibromides gave *trans*- and *cis*-olefins, respectively (≥98% stereoselectivity

(7) Engman, L.; Persson, J.; Andersson, C. M.; Berglund, M. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1309−1314.

(8) (a) Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 793 and 897. (b) Irgolic, K. J. In *Houben-Weyl Methoden der Organischen Chemie: Organotellurium Chemistry*; Klamann, D., Ed.; Georg Thieme: New York, 1990; Vol. E12b.

(9) Detty, M. R.; Friedman, A. E.; McMillan, M. *Organometallics* **1995**, *14*, 1442−1449.

as determined by ^{1}H NMR). Debromination of *erythro*-1,2-dibromo-1-phenylpropane with **9** gave 95% conversion in $CDCl_3$ to *trans*-1-phenylpropene and Te(IV) dibromide **10** after 24 h at 100 °C (entry 2, Table 1). Debromination of *erythro*-5,6-dibromodecane with **9** was slower, giving 60% conversion in $CDCl_3$ to *trans*-5-decene and Te(IV) dibromide **10** after 144 h at 100 °C (entry 4, Table 1). Debromination of *threo*-2,3-dibromopentane with either **1** or **9** was much slower with only 15% conversion to *cis*-2-pentene and **10** after 240 h in $CDCl_3$ at 100 °C (entry 6, Table 1). The debromination of *threo*-2,3-dibromo-4-methylpentane with either **1** or **9** was also slow at 100 °C with only 5% conversion to *cis*-4-methyl-2-pentene after 153 h (entry 7, Table 1).

Debromination of 1,2-dibromodecane with **9** gave 61% conversion to 1-decene and **10** after 240 h in $CDCl_3$ at 100 °C (entry 5, Table 1).

Both *trans*-1,2-dibromocyclohexane and *trans*-1,2-dibromocycloheptane gave a slow thermal loss of bromine in the absence of a telluride reagent. The addition of **9** to *trans*-1,2-dibromocyclohexane (entry 8, Table 1) did not appreciably accelerate the rate of appearance of the cyclohexene (≈15% conversion after 300 h at 100 °C) relative to the thermal reaction. However, the addition of telluride **9** to *trans*-1,2-dibromocycloheptane (entry 9, Table 1) gave cycloheptene at a rate comparable to that observed for the debromination of *erythro*-5,6-dibromodecane.

C. Reaction Order and Kinetics. The kinetics of debromination of 2,3-dibromo-2-methylpentane and *erythro*-5,6-dibromodecane with **9** were followed by ^{1}H NMR spectroscopy. For these systems, the olefinic protons, protons on carbons bearing bromine in the *vic*-dibromides, and α-methylene protons of telluride **9** were well separated at 300 MHz. Residual $CHCl_3$ was used as an internal standard. The debromination/bromination equilibria complicate kinetic analysis in these systems, especially for *erythro*-5,6-dibromodecane, as does the exchange of bromine between **9** and **10**.[10] As a consequence, we chose to examine initial rates of reaction in these systems.

Stock solutions of 0.20 M **9** and 0.20 M 2,3-dibromo-2-methylpentane or *erythro*-5,6-dibromodecane were prepared in $CDCl_3$. The stock solution and 2- (0.1 M) and 4-fold (0.05 M) dilutions were sealed in NMR tubes and placed in a constant temperature bath at 90 °C. The solutions were sampled periodically over the initial 20% of reaction for 2,3-dibromo-2-methylpentane and over the initial 10% of reaction for *erythro*-5,6-dibromodecane. The initial reaction velocities are compiled in Table 2. The observed ratios are close to 16:4:1 for each system and suggest an overall second-order reaction.

Second-order rate constants for these two systems were approximated under pseudo-first-order conditions (telluride **9** in excess at 0.50, 0.30, and 0.10 M, dibromide concentration constant at 0.025 M) for initial rates of reaction in $CDCl_3$ at 90 °C as before (Table 2). The observed rates were plotted as a function of telluride concentration to give second-order rate constants for debromination with **9** of $(2.28 \pm 0.08) \times 10^{-4}$ M^{-1} s^{-1} for 2,3-dibromo-2-methylpentane and $(4.37 \pm 0.02) \times 10^{-6}$ M^{-1} s^{-1} for *erythro*-5,6-dibromodecane at 90 °C in $CDCl_3$ (Figure 1).

(10) Detty, M. R.; Friedman, A. E.; McMillan, M. *Organometallics* **1994**, *13*, 3338−3345.

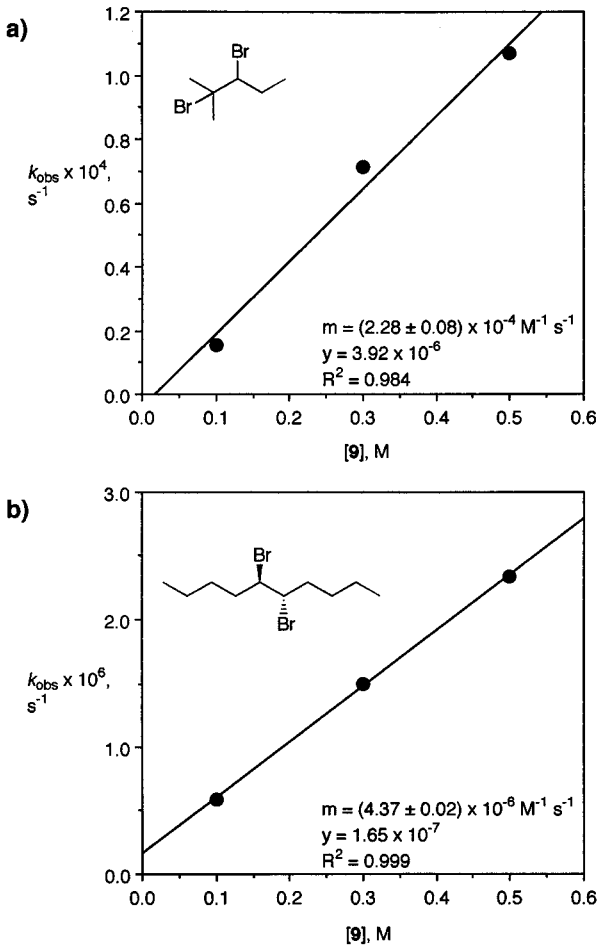
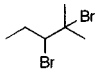
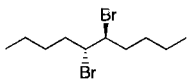


Figure 1. Plot of pseudo first-order rate constants as a function of telluride **9** concentration (0.50, 0.30, and 0.10 M) for (a) 2,3-dibromo-2-methylpentane (0.025 M) and (b) *erythro*-5,6-dibromodecane (0.025 M). The slopes of the least-squares linear fit of the data described second-order rate constants for olefin formation of (a) $(2.28 \pm 0.08) \times 10^{-4}$ M^{-1} s^{-1} for 2,3-dibromo-2-methylpentane and (b) $(4.37 \pm 0.02) \times 10^{-6}$ M^{-1} s^{-1} for *erythro*-5,6-dibromodecane at 90 °C in $CDCl_3$.

Table 2. Initial Reaction Velocities (v) for Olefin Formation for the Reaction of Telluride 9 and *vic*-Dibromide Substrates at (90 ± 1) °C in $CDCl_3$

	[**9**], M	[dibromide], M	v_{init}, M s^{-1}	v_{rel}	k_{obs}, s^{-1}
	0.20	0.20	9.48×10^{-6}	13	
	0.10	0.10	2.74×10^{-6}	3.5	
	0.050	0.050	7.80×10^{-7}	1	
	0.50	0.025			1.07×10^{-4}
	0.30	0.025			7.13×10^{-5}
	0.10	0.025			1.56×10^{-5}
	0.20	0.20	1.46×10^{-7}	16	
	0.10	0.10	3.08×10^{-8}	3.3	
	0.050	0.050	9.27×10^{-9}	1	
	0.50	0.025			2.34×10^{-6}
	0.30	0.025			1.50×10^{-6}
	0.10	0.025			5.91×10^{-7}

The results suggest a first-order dependence in both telluride and *vic*-dibromide for the debromination reaction. The overall rate expression for loss of bromide can be expressed as:

$$-\mathrm{d[dibromide]}/\mathrm{d}t = C\mathrm{[bromide][telluride]} \quad (3)$$

D. Effects of Solvent Polarity on Rates. Under pseudo-first-order conditions, the rates of debromination

are faster in the more polar CD_3CN. For 2,3-dibromo-2-methylpropane and **9**, the second-order rate constant is $(2.28 \pm 0.08) \times 10^{-4}$ M^{-1} s^{-1} in $CDCl_3$ and is $(6.1 \pm 0.1) \times 10^{-4}$ M^{-1} s^{-1} in CD_3CN at 90 °C. For *erythro*-5,6-dibromodecane and **9**, the second-order rate constant is $(4.37 \pm 0.02) \times 10^{-6}$ M^{-1} s^{-1} in $CDCl_3$ at 90 °C and is $(1.71 \pm 0.05) \times 10^{-5}$ M^{-1} s^{-1} in CD_3CN at 90 °C.

E. Competition Experiments. To establish relative rates of reaction for various dibromide substrates, we set up competition experiments between equimolar concentrations (0.10 M) of pairs of dibromides with similar reactivity toward telluride **9**, which was the limiting reagent (0.05 M). The relative rates were determined both in $CDCl_3$ and CD_3CN at 90 °C, and results obtained from these experiments are compiled in Table 1.

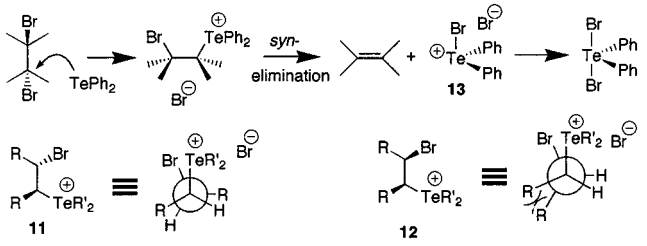
The relative reactivities of 2,3-dibromo-2-methylpentane (entry 3, Table 1) and *erythro*-5,6-dibromodecane (entry 4) in the two solvents are listed as the ratios of their second-order rate constants (52:1 in $CDCl_3$ and 35:1 in CD_3CN). As a check on the kinetics, competition experiments between the two substrates gave roughly 15:1 ratios of 2-methyl-2-pentene to *trans*-5-decene both in $CDCl_3$ and in CD_3CN.

Competition between 1,2-dibromo-2-methyl-1-phenylpropane (entry 1, Table 1) and 2,3-dibromo-2-methylpentane (entry 3, Table 1) gave 2-methyl-1-phenylpropene and 2-methyl-2-pentene, respectively, in a 76:24 ratio after 5 h in $CDCl_3$ and in a 70:30 ratio after 2 h in CD_3CN. Competition between 1,2-dibromo-2-methyl-1-phenylpropane and *erythro*-1,2-dibromo-1-phenylpropane (entry 2, Table 1) gave 2-methyl-1-phenylpropene and *trans*-1-phenylpropene, respectively, in a 52:48 ratio after 24 h in $CDCl_3$. Competition between *erythro*-5,6-dibromodecane and 1,2-dibromodecane (entry 5, Table 1) gave *trans*-5-decene and 1-decene, respectively, in a 67:33 ratio in $CDCl_3$ after 24 h and in a 73:27 ratio in CD_3CN after 24 h.

Competition between *erythro*-5,6-dibromodecane and *threo*-2,3-dibromopentane (entry 6, Table 1), *threo*-2,3-dibromo-4-methylpentane (entry 7), and *trans*-1,2-dibromocyclohexane (entry 8) gave *trans*-5-decene as the only characterizable product after 24 h in either $CDCl_3$ or CD_3CN. We have assigned the ratio of *trans*-decene to *cis*-2-pentene, *cis*-4-methyl-2-pentene, cyclohexene, or cycloheptene to be ≥ 20:1 on the basis of the integrals of the appropriate olefinic regions of the ^1H NMR spectra of the mixtures. Competition between *erythro*-5,6-dibromodecane and *trans*-1,2-dibromocycloheptane (entry 9) gave a 50:50 ratio of olefins (after correction for the thermal process with *trans*-1,2-dibromocycloheptane).

F. Mechanism of Reaction. Nucleophilic Attack at Carbon (Telluronium Model). A mechanistic explanation of the debromination of *vic*-dibromides with diorganotellurides must account for several observations: (1) the reaction is highly stereoselective with *erythro*-dibromides giving *trans*-olefins and *threo*-dibromides giving *cis*-olefins, (2) the reaction is accelerated by more electron-rich diorganotellurides, (3) the reaction is accelerated in a more polar solvent, (4) the reaction is accelerated by the addition of carbocation-stabilizing substituents to the carbons bearing the bromo substituents, and (5) *erythro*-dibromides are much more reactive than *threo*-dibromides. Furthermore, the reaction was second-order overall and no intermediate species were observed.

Scheme 1



Campos, Petragnani, and Thomé observed telluronium salts in the reaction of diphenyl telluride (**3**) with 1,2-dibromoethane.[4] If telluronium salts were intermediates, then debromination might follow the mechanism shown in Scheme 1. S_N2 attack by the Te atom of a diorganotelluride at a C−Br bond of substrate would lead to inversion of configuration at the substrate carbon and would account for the overall second-order kinetics and first-order dependence in both telluride and dibromide. More electron-rich tellurides should also be more nucleophilic which is consistent with the experimental observations. Furthermore, the formation of the telluronium salts should be accelerated in more polar solvents.

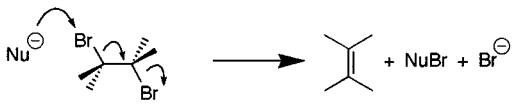
The *erythro*-dibromides would produce *threo*-telluronium salts **11** while *threo*-dibromides would produce *erythro*-telluronium salts **12**. The differences in rates and product distributions between *threo*- and *erythro*-dibromides requires that loss of the second halide must proceed in such a manner to allow control of olefin stereochemistry and must avoid a common intermediate from the two diastereomers. A concerted *syn*-elimination of a bromotelluronium salt **13** would differentiate the *threo*- and *erythro*-diastereomers, and the stereochemistry of the olefinic product would be defined by the stereochemistry of the telluronium salt intermediate. The addition of bromide to telluronium salts **13** would give the Te(IV) derivatives. Oxidative addition of bromine or iodine to diorganotellurides produces intermediates similar to **13**, which have been detected by stopped-flow spectroscopy.[9,11] Collapse of the bromotelluronium bromide salts **13** to neutral Te(IV) derivatives such as **5**−**8** and **10** has also been observed by stopped-flow spectroscopy.[9,11]

A concerted *syn*-elimination from intermediate **11** would generate a *trans*-olefin. A concerted *syn*-elimination from **12** to generate a *cis*-olefin would be disfavored relative to **11** due to the eclipsing interactions of the two R groups. Consistent with this proposal is the observation that debromination of *threo*-2,3-dibromopentane is somewhat faster than that of *threo*-2,3-dibromo-4-methylpentane (increased steric interactions). The slow debromination of the *trans*-1,2-dibromocycloalkanes may reflect not only increased steric interactions but also increased ring strain for *syn*-eliminations in the cyclic molecules.

While this model explains the observed stereoselectivity, the electronic effects at tellurium, the overall second-order behavior, the effects of solvent polarity, and the relative rates of debromination of *erythro*- and *threo*-dibromides, *it fails to explain the relative rates of reaction*

(11) (a) Nefedov, V. D.; Sinotova, E. N.; Sarbash, A. N.; Kolobov, E. A.; Kapustin, V. K. *Radiokhimiya* **1971**, *13*, 435−437. (b) Nefedov, V. D.; Sinotova, E. N.; Sarbash, A. N.; Timofev, S. A. *Radiokhimiya* **1969**, *11*, 1545−155. (c) Detty, M. R.; Luss, H. R. *Organometallics* **1986**, *5*, 2250−2258.

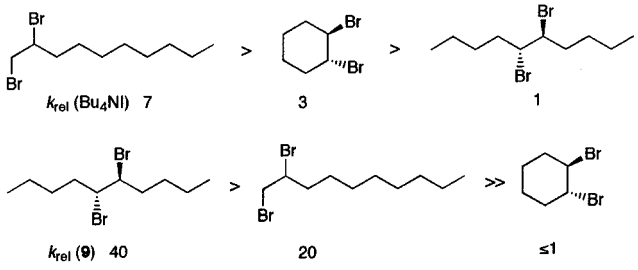
Scheme 2



(Table 1) for the substrates. One would expect 1,2-dibromodecane to be the most reactive substrate in this series both to nucleophilic attack by the telluride and to *syn*-elimination from an intermediate telluronium salt due to the minimal steric interactions. Instead, the reactivity order appears to be that expected from formation of carbocation or related intermediates.

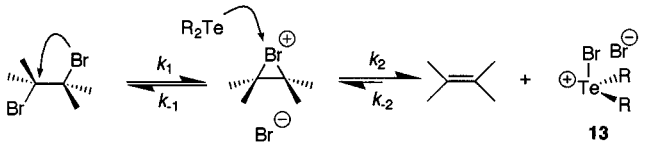
Nucleophilic Attack at Bromide (Iodide Model). Debrominations of *vic*-dibromides with either sodium 2-thienyl telluride[3f] or iodide[3a,b] have been proposed to occur through the mechanism illustrated in Scheme 2. In this model, direct attack of the nucleophile on bromine leads to olefin via an E2-like process. One can propose a similar mechanism for debrominations with diorganotellurides although one might expect slower reaction from an uncharged nucleophile relative to anionic nucleophiles.

The mechanism of Scheme 2 is not a likely pathway in the debrominations with diorganotellurides if one considers relative rates of reaction. Substrates such as 1,2-dibromodecane would be expected to be more reactive than dibromides from internal olefins if this mechanism were operative due to reduced steric hindrance. In fact, competition experiments involving debromination of 1,2-dibromodecane, *erythro*-5,6-dibromodecane, and *trans*-1,2-dibromocyclohexane with Bu_4NI gave the relative reactivities indicated below with 1,2-dibromodecane more reactive than *trans*-1,2-dibromocyclohexane which in turn is more reactive than *erythro*-5,6-dibromodecane. This order of reactivity is in marked contrast to the relative reactivity of the same three substrates toward dihexyl telluride (**9**) in which *trans*-1,2-dibromocyclohexane is relatively inert while *erythro*-5,6-dibromodecane is twice as reactive as 1,2-dibromodecane. These results suggest that different mechanistic pathways are involved with iodide and diorganotellurides.



Bromonium Ion Model. Neighboring group participation in substitution reactions of *vic*-dibromides have been described for dibromides derived from cholesterol, cholest-5-ene, and 5α-cholest-2-ene.[12] In these systems, thermal rearrangement of *trans*-diaxial dibromides to *trans*-diequatorial dibromides were observed. While discrete bromonium ion intermediates were not proposed, tight ion pairs or bridging intermediates involving partial positive and partial negative charges were suggested to explain the rearrangements.

Scheme 3



Neighboring group participation in the solvolysis of the *vic*-dibromides of this study as shown in Scheme 3 offers a mechanistic picture that accounts for the observed experimental details. Loss of bromide is assisted by the formation of a bromonium ion intermediate, which can collapse back to the *vic*-dibromide. The diorganotelluride functions as a scavenger of the positive bromine to give the bromotelluronium salt **13** and the olefin. The relative rates observed in $CDCl_3$ and CD_3CN are consistent with formation of a positively charged intermediate with some charge on carbon. Bromonium ion formation would give the stereoselectivity observed for *erythro*- and *threo*-dibromides by forming a bridged, nonrotating intermediate. Eclipsing interactions would decrease the stability as well as the rate of formation of bromonium ions derived from *threo*-dibromides relative to *erythro*-dibromides. In this model, 1,2-dibromodecane would be expected to be slower than more highly substituted analogues since an intermediate bromonium ion (or carbocation) would lack stabilizing substituents. More polar solvents should accelerate the rate of bromonium ion formation while more electron-rich diorganotellurides should both accelerate the debromination and drive the equilibrium to the right.

In bromination reactions of olefins that can form benzylic carbocations, loss of stereospecificity has been observed.[13] Similar loss of stereoselectivity might be expected from *vic*-dibromides with a phenyl substituent or a tertiary center.

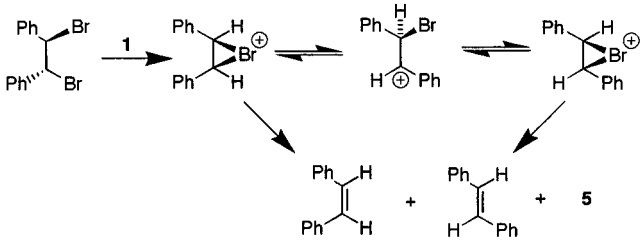
Debromination of *threo*-1,2-Dibromo-1,2-diphenylethane. Debromination of *erythro*-1,2-dibromo-1,2-diphenylethane was highly stereoselective to give *trans*-stilbene. Bromonium ion formation would lead to minimal steric interactions and would produce the thermodynamically favored *trans*-olefin. Debromination of *threo*-1,2-dibromo-1,2-diphenylethane did not show the same stereoselectivity. In refluxing $CDCl_3$, *threo*-1,2-dibromo-1,2-diphenylethane (0.10 M) and diaryl telluride **1** (0.10 M) gave a 40:60 mixture of *cis*:*trans*-stilbenes (96% conversion) in addition to formation of Te(IV) dibromide **5** after 2 h (Scheme 4). At ambient temperature, only *trans*-stilbene was formed in 96% yield after 15 h. At the higher temperature, essentially no stereoselectivity was observed while at ambient temperature the thermodynamically more stable *trans*-olefin was formed.

Unlike the *erythro*-isomer which gave only *trans*-stilbene (the thermodynamic product and expected product from bromonium ion participation), neighboring group participation in *threo*-1,2-dibromo-1,2-diphenylethane would lead to steric repulsion between the eclipsed

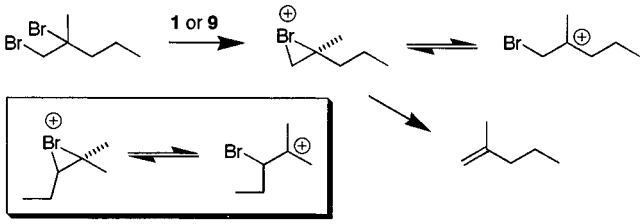
(12) (a) Grob, C. A.; Winstein, S. *Helv. Chim. Acta* **1952**, *35*, 782. (b) Kwart, H.; Weisfeld, L. B. *J. Am. Chem. Soc.* **1956**, *78*, 635. (c) Barton, D. H. R.; King, J. F. *J. Chem. Soc.* **1958**, 4398. (d) Alt, G. H.; Barton, D. H. R. *J. Chem. Soc.* **1954**, 4284. (d) Barton, D. H. R.; Rosenfelder, W. J. *J. Chem. Soc.* **1951**, 1048.

(13) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469−1476. (b) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1477−1483.

Scheme 4



Scheme 5



phenyl groups (Scheme 4). While neighboring group participation probably assists the initial solvolysis, the bromonium ion formed would have weaker C−Br bonds because of the phenyl-stabilized cationic centers. Ring opening followed by rotation would lead to the more stable *trans*-bromonium ion intermediate and *trans*-stilbene upon debromination. At the more elevated temperature, a mixture of both isomers is produced while at ambient temperature only the more stable *trans*-isomer is observed.

Bromonium Ions vs Carbocations. The production of a mixture of *cis*- and *trans*-stilbene in Scheme 4 raises the question of whether debromination might not occur from the carbocation intermediate (via an E2-like attack of telluride at bromine) of Scheme 4 rather than from a bromonium ion intermediate. 1,2-Dibromo-2-methylpentane is perhaps a better system for differentiating a carbocation mechanism from a bromonium ion mechanism as shown in Scheme 5. Bromonium ion formation in this substrate is perhaps less favored relative to formation of a tertiary carbocation since a bromonium ion intermediate would be highly unsymmetrical with contributions from a primary and a tertiary cationic center as shown in Scheme 5. Products derived from formation of the tertiary carbocation might be expected from 1,2-dibromo-2-methylpentane. Interestingly, debromination of 1,2-dibromo-2-methylpentane with either **1** or **9** gave, in addition to 7% 2-methyl-1-pentene after 240 h at 100 °C in $CDCl_3$, 30% dehydrobromination to a mixture of bromoalkenes derived from the tertiary carbocation of Scheme 5 (*m*/*z* 162 for $C_6H_{11}{}^{79}Br$). Products derived from the tertiary carbocation are the major products. This is in marked contrast to the debromination of 2,3-dibromo-2-methyl pentane with **1** or **9**, which gives 95% olefin in a much shorter time frame. The bromonium ion and tertiary carbocation from this system are shown in Scheme 5 as well.

One might expect both tertiary carbocations of Scheme 5 to be similarly susceptible to loss of "Br^+" to give debromination and to loss of a proton to give dehydrobromination. No products of dehydrobromination were observed in the debrominations of 2,3-dibromo-2-methylpentane, which suggests that 1,2-dibromo-2-methylpentane gives dehydrobromination via a different intermediate than the debromination path.

The bromonium ion mechanism for debromination must account for the second-order rate expression of eq 3 for the reaction as well as the first-order dependence in both dibromide and telluride. Bromination of olefins is driven far to the side of the *vic*-dibromide product. As depicted in Scheme 3, the reverse reaction of bromonium ion formation (most likely formed as a tight ion pair) is highly favored with $k_{-1} \gg k_1$. Any reagent scavenging "Br^+" from a bromonium ion intermediate is competing with k_{-1}. Stopped-flow studies on the rates of reaction of diorganotellurides with bromine and iodine show second-order rate constants which are $\geq 10^8$ M^{-1} s^{-1} for formation of the η_1-complex for bromine and tellurium and $\geq 10^6$ M^{-1} s^{-1} for iodine.[8,9,12] While telluride scavenging of positive bromine from a bromonium ion intermediate may not be as fast as reaction with free halogen, the k_2[telluride] term of Scheme 3 should certainly be large relative to k_1 for the dissociation of the *vic*-dibromide but then must compete with a large k_{-1} under these reaction conditions. A preequilibrium involving bromonium ion and *vic*-dibromide followed by telluride scavenging of "Br^+" would give a reaction that appears to be first order in both dibromide and telluride and second-order overall.

From microscopic reversibility, the formation of the bromonium ion is certainly reversible and ionization is expressed by k_1/k_{-1} (or K_1, assuming a tight ion pair) in Scheme 3. The constant *C* expressed in eq 3 is actually the product k_2K_1 for initial rates of reaction. It should be noted that the addition of 3 equiv of LiBr to the reaction mixtures had little effect on the rates of reaction of 2,3-dibromo-2-methylpentane or *erythro*-5,6-dibromodecane with **9**. This suggests that "free" (highly solvated) bromonium ion and bromide are not involved and that tight ion pairs are more likely intermediates.

Summary and Conclusions

Diorganotellurides are selective reagents for the debromination of *vic*-dibromide precursors to phenyl-substituted or trisubstituted olefins in the presence of less highly substituted *vic*-dibromides. The effects of substitution suggest that the reaction progresses through the development of cationic character, perhaps involving the formation of cyclic bromonium ion intermediates. The equilibria involved in this process (dibromide/telluride vs olefin/Te(IV) dibromide; Te−Br exchange reactions) limit their utility. In the accompanying paper,[14] we describe a debromination process that is catalytic in diorganotelluride and drives debrominations to completion.

Experimental Section

General Methods. Solvents (acetone, chloroform, dichloromethane, ethyl acetate, hexanes), deuteriochloroform, deuterioacetonitrile, magnesium sulfate, *trans*-stilbene, *cis*-stilbene, *trans*-3-hexene, *cis*-4-methyl-2-pentene, *trans*-5-decene, 1-decene, *trans*-1-phenylpropene, *cis*-2-pentene, 2-methyl-1-phenylpropene, 2-methyl-2-pentene, cyclohexene, and cycloheptene were used as received from Aldrich Chemical Co. Tellurides **1**−**4** and dibromides **5**−**8** were prepared according to ref 5. Preparative reactions were stirred magnetically.

(14) Butcher, T. S.; Detty, M. R. *J. Org. Chem.* **1998**, *63*, 175−178.

Concentration in vacuo was performed on a Büchi rotary evaporator. Nuclear magnetic resonance (NMR) spectra were recorded at 30.0 °C on a Varian Gemini-300 instrument with residual solvent signal as internal standard: $CDCl_3$ (δ 7.26 for proton, δ 77.0 for carbon).

Preparation of Di-*n*-hexyl Telluride (9).[7b] Sodium borohydride (1.9 g, 0.050 mol) was added in three portions every 15 min to a refluxing slurry of tellurium powder (2.55 g, 0.020 mol) in 50 mL of 0.3 M sodium ethoxide in ethanol under an inert atmosphere of argon. After the tellurium was consumed, a chalky white mixture was obtained. 1-Bromohexane (6.6 g, 0.040 mol) in 20 mL of ethanol was added. The reaction mixture was stirred for 3 h at ambient temperature. The mixture was then poured into water, and the product was extracted with hexanes (3 × 50 mL). The combined organic extracts were washed with brine, filtered through Celite, dried over $MgSO_4$, and concentrated. The reside was purified via short-path distillation at 100−102 °C (0.05 Torr) to give **9**[7b] as a light orange oil (3.32 g, 56% yield): ^{1}H NMR ($CDCl_3$) δ 2.60 (t, 4 H, J = 7.7 Hz), 1.71 (quintet, 4 H, J = 7.5 Hz), 1.32 (m, 12 H), 0.88 (t, 6 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 32.19, 31.73, 31.20, 22.57, 14.03, 3.22; FDMS, *m*/*z* 300 ($C_{12}H_{26}{}^{130}Te$).

Preparation of Dibromo Di-*n*-hexyl Tellurium(IV) (10).[7b] Dihexyl telluride (**3**, 596 mg, 2.00 mmol) was dissolved in acetone (10 mL). A 2.5-mL aliquot of a 1.0 M solution of bromine in $CHCl_3$ was added dropwise, and the resulting solution was stirred for 15 min at ambient temperature. The reaction mixture was concentrated to give **10** as a dark brown oil (0.855 g, 93.3%): ^{1}H NMR ($CDCl_3$) δ 3.61 (t, 4 H, J = 7.7 Hz), 2.14 (quintet, 4 H, J = 7.1 Hz), 1.47 (m, 4 H), 1.34 (m, 8 H), 0.88 (t, 6 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 45.29, 31.08, 30.71, 25.76, 22.40, 13.98; FDMS, *m*/*z* 458 ($C_{12}H_{26}{}^{130}Te^{79}Br_2$).

Preparation of Substrates. The known *vic*-dibromide substrates were all prepared from brominations of commercially available mono-, di-, and trisubstituted olefins: *erythro*-1,2-dibromo-1,2-diphenylethane from *trans*-stilbene,[13] *threo*-1,2-dibromo-1,2-diphenylethane from *cis*-stilbene,[13] *erythro*-1,2-dibromo-1-phenylpropane from *trans*-1-phenylpropene,[13] 1,2-dibromodecane from 1-decene,[3i] *erythro*-3,4-dibromohexane from *trans*-3-hexene,[15] *erythro*-5,6-dibromodecane from *trans*-5-decene,[15] *threo*-2,3-dibromopentane from *cis*-2-pentene,[16] *threo*-2,3-dibromo-4-methylpentane from *cis*-4-methyl-2-pentene,[17] 1,2-dibromo-2-methyl-1-phenylpropane from 2-methyl-1-phenylpropene,[18] 2,3-dibromo-2-methylpentane from 2-methyl-2-pentene,[19] *trans*-1,2-dibromocyclohexane from cyclohexene,[20] *trans*-1,2-dibromocycloheptane from cycloheptene,[15] and 1,2-dibromo-2-methylpentane from 2-methyl-1-pentene.[15]

In a typical procedure, bromine (1.68 g, 10.5 mmol) in 30 mL of $CHCl_3$ was added dropwise to a stirred solution of substrate (10 mmol) in 30 mL of $CHCl_3$ at ambient temperature in the dark (3 h to 7 days).[15] The reaction mixture was washed with saturated $NaHSO_3$ solution. The organic layer was separated, dried over $MgSO_4$, and concentrated. The dibromide was recrystallized (EtOAc/hexanes) for *threo*- and *erythro*-1,2-dibromo-1,2-diphenylethane and was distilled (bulb-to-bulb, 0.1 Torr) for the other substrates. The diastereomeric purity of the *vic*-dibromides was established by ^{1}H and ^{13}C NMR.

For *erythro*-3,4-dibromohexane: ^{1}H NMR ($CDCl_3$) δ 4.12 (m, 2 H), 2.08 (m, 2 H), 0.90 (t, 6 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 59.96, 36.64, 13.95; FDMS *m*/*z* 242 ($C_6H_{12}{}^{79}Br_2$).

For *threo*-2,3-dibromo-4-methylpentane: ^{1}H NMR ($CDCl_3$) δ 4.31 (dxq, 1 H, J = 3.3, 6.7 Hz), 3.71 (dxd, 1 H, J = 3.3, 6.8 Hz), 2.08 (m, 1 H), 1.73 (d, 3 H, J = 6.7 Hz), 1.06 (d, 3 H, J = 6.5 Hz), 0.98 (d, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 69.88, 52.23, 34.18, 25.58, 21.29, 20.71; FDMS *m*/*z* 242 ($C_6H_{12}{}^{79}Br_2$).

For *erythro*-1,2-dibromo-1,2-diphenylethane: mp 226−228 °C (lit[15] mp 237−239 °C); ^{1}H NMR ($CDCl_3$) δ 7.50 (m, 4 H),7.43 (m, 2 H), 7.38 (m, 4 H), 5.46 (s, 2 H); FDMS *m*/*z* 338 ($C_{14}H_{12}{}^{79}Br_2$).

For *threo*-1,2-dibromo-1,2-diphenylethane: mp 108.5−110.0 °C (lit[15] mp 110−111 °C), ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 10 H), 5.45 (s, 2 H); FDMS *m*/*z* 338 ($C_{14}H_{12}{}^{79}Br_2$).

For *erythro*-1,2-dibromo-1-phenylpropane: ^{1}H NMR ($CDCl_3$) δ 7.31−7.43 (m, 5 H), 5.04 (d, 1 H, J = 10.2 Hz), 4.61 (m, 1H), 2.04 (d, 3 H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 140.60, 128.81, 128.67, 127.76, 59.22, 51.19, 25.86; FDMS *m*/*z* 276 ($C_9H_{10}{}^{79}Br_2$).

For 1,2-dibromodecane: ^{1}H NMR ($CDCl_3$) δ 4.14 (m, 1 H), 3.82 (dxd, 1 H, J = 4.1, 10.0 Hz), 3.60 (t, 1 H, J = 10.0 Hz, 2.11 (m, 1 H), 1.76 (m, 1 H), 1.55 (m, 1 H), 1.40 (m, 1 H), 1.26 (br s, 10 H), 0.86 (t, 3 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 53.10, 36.33, 36.06, 31.84, 29.37, 29.20, 28.84, 26.77, 22.66, 14.10; FDMS *m*/*z* 298 ($C_{10}H_{20}{}^{79}Br_2$).

For *erythro*-5,6-dibromodecane: ^{1}H NMR ($CDCl_3$) δ 4.12 (m, 2 H), 2.08 (m, 2 H), 1.92 (m, 2 H), 1.54 (m, 2 H), 1.2−1.5 (m, 6 H), 0.90 (t, 6 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 59.96, 36.64, 29.12, 22.07, 13.95; FDMS *m*/*z* 298 ($C_{10}H_{20}{}^{79}Br_2$).

For *threo*-2,3-dibromopentane: ^{1}H NMR ($CDCl_3$) δ 4.41 (qxd, 1 H, J = 3, 7 Hz), 4.07 (txd, 1 H, J = 3, 10 Hz),2.10 (m, 1 H), 1.80 (m, 1 H), 1.72 (d, 3 H, J = 7 Hz), 1.04 (t, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 62.22, 52.26, 27.54, 21.66, 12.72; FDMS *m*/*z* 228 ($C_5H_{10}{}^{79}Br_2$).

For 2,3-dibromo-2-methylpentane: ^{1}H NMR ($CDCl_3$) δ 4.08 (d, 1 H, J = 11 Hz), 2.43 (m, 1 H), 1.73 (m, 1 H), 1.94 (s, 3 H), 1.76 (s, 3 H), 1.10 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 69.18, 68.59, 35.55, 29.29, 28.19, 13.43; FDMS *m*/*z* 242 ($C_6H_{12}{}^{79}Br_2$).

For 1,2-dibromo-2-methylpentane: ^{1}H NMR ($CDCl_3$) δ 3.85 (d, 1 H, J = 10.2 Hz), 3.77 (d, 1 H, J = 10.2 Hz), 1.83 (m, 1 H), 1.82 (s, 3 H), 1.50 (m, 2 H), 1.12 (m, 1 H), 0.94 (t, 3 H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 67.98, 44.40, 42.53, 30.65, 18.87, 13.90; FDMS *m*/*z* 242 ($C_6H_{12}{}^{79}Br_2$).

General Procedure for Debrominations of *vic*-Dibromides. The substrate (0.10 mmol) and diorganotelluride (0.10 mmol, 36 mg for **1**, 30 mg for **9**) were dissolved in 1.0 mL of $CDCl_3$ in a 5-mm NMR tube. The tube was sealed, and resulting solution was placed in a thermostated bath at 90−100 °C as indicated. The samples were examined periodically by ^{1}H NMR using residual $CHCl_3$ as an internal standard until no further change in the ratio of products was observed.

The olefins were identified in the reaction mixture from their ^{1}H NMR and ^{13}C NMR spectra, which were superimposable on the spectra of authentic samples (Aldrich).

General Procedure for Competition Experiments. The *vic*-dibromides (0.20 mmol each) and telluride **9** (30.0 mg, 0.10 mmol) were dissolved in 2.0 mL of $CDCl_3$ or CD_3CN. The resulting solutions were placed in 5-mm NMR tubes (1 mL in each) and were immersed in a constant temperature bath at 90 °C. After the indicated times, product ratios were measured by ^{1}H NMR spectroscopy and averaged for duplicate runs.

General Procedure for Kinetics Experiments. A stock solution of 0.80 mmol each of dibromide and telluride **9** in 4.0 mL of $CDCl_3$ (0.20 M in each reagent) was prepared. Dilution (2- and 4-fold) of the stock solution gave a series with concentrations of 0.20, 0.10, and 0.050 M in each reagent. The solutions were immersed in a constant temperature bath at (90 ± 1) °C and were sampled periodically over the initial reaction. A plot of $[A]_t/[A_0]$ as a function of time gave initial slopes of $-(4.89 \pm 0.06) \times 10^{-5}$ s^{-1} at 0.20 M reagents, $-(2.74 \pm 0.04) \times 10^{-5}$ s^{-1} at 0.10 M reagents, and $-(1.56 \pm 0.05) \times 10^{-5}$ s^{-1} at 0.05 M reagents for 2,3-dibromo-2-methylpentane and slopes of $-(7.50 \pm 0.05) \times 10^{-7}$ s^{-1} at 0.20 M reagents, $-(3.1 \pm 0.1) \times 10^{-7}$ s^{-1} at 0.10 M reagents, and $-(1.86 \pm 0.04) \times 10^{-7}$ s^{-1} at 0.05 M reagents for *erythro*-5,6-dibromodecane.

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The initial slopes were multiplied by $[\mathbf{9}]_0$ to give the reaction velocities in Table 2.

For pseudo-first-order reactions, 0.5, 0.3, and 0.1 mmol samples of telluride **9** (0.149, 0.0894, and 0.0149 g, respectively) were weighed into 5-mm NMR tubes. To each of these samples was added 1.0 mL of a 0.05 M solution of dibromide in either $CDCl_3$ or CD_3CN. The NMR tubes were sealed and immersed in a constant temperature bath at (90 ± 1) °C. The samples were monitored periodically by ^1H NMR over the first 1−2 half-lives of reaction. The observed rates (k_{obs}, Table 2) were plotted as a function of [**9**] as shown in Figure 1 to give the apparent second-order rate constants.

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