Articles

Conversion of Aziridinemethanol Sulfonate Esters to Allylic Amines via Tellurium Chemistry[1]

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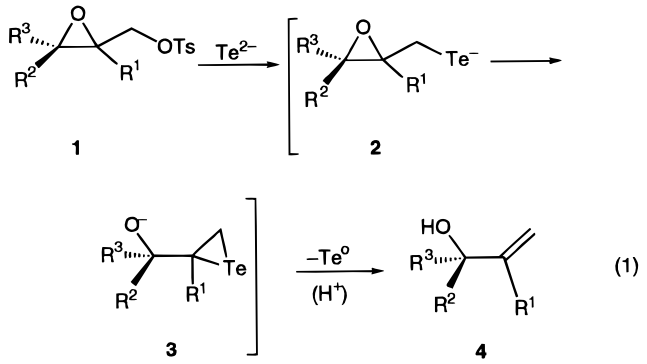
Sulfonate esters of aziridinemethanols are converted to allylic amines by treatment with telluride ion obtained by reduction of elemental tellurium. In the course of the reaction, tellurium(0) is reformed and may be reused, thus removing the need to dispose of a key reagent. The telluride reaction yields optically active allylic amines from optically active aziridinemethanols. In contrast to many ring-openings of aziridines by nucleophiles, activation by an electron-withdrawing substituent on nitrogen is not necessary and is even detrimental.

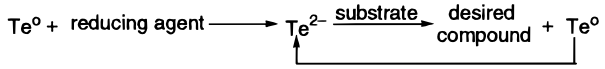
Recently, the conversion of sulfonate esters of oxiranemethanols, **1**, to useful allylic alcohols **4** via putative intermediates **2** and **3** has been effected under mild conditions by taking advantage of the high nucleophilicity of telluride ion and the thermodynamic instability of the latter with respect to the element (eq 1).[2] The process is



(1)

shown in Scheme 1 and has been termed a "nucleophilic reduction".[3] Reactions of this type are environmentally benign because (1) the relatively nontoxic elemental tellurium[4] can be recovered and reused, (2) aqueous media can be employed in the reduction of tellurium, (3) the process can occur in the solid phase, eliminating the need for a reaction solvent,[5] and (4) the tellurium can be used in catalytic amounts as long as a stoichiometric quantity of reducing agent is present to maintain the concentration of telluride ion (Scheme 1).[2h] Other substrates that behave according to Scheme 1 are cyclic sulfates and thionocarbonates of 1,2-diols that yield alkenes stereospecifically.[6]

Scheme 1[7]



This paper reports some results in extension of the tellurium process of Scheme 1 to aziridinemethanol analogues of the oxiranemethanols. The allylic amines that would be formed are important synthetic intermediates, particularly if they are chiral. For example, conversions to α- or *β*-amino acids by oxidation of the carbon−carbon double bond are useful transformations.[8] A variety of methods exist for the synthesis of allylic amines,[9] and numerous recent investigations on their preparation attest to their current significance.[8−10]

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(1) (a) Taken from: Pepito, A. S. Ph.D. Thesis, Syracuse University, May 1996. (b) A preliminary report: Pepito, A. S.; Dittmer, D. C. *Abstracts of Papers*, 209th National Meeting of the American Chemical Society, Anaheim, CA, Apr 2−6, 1995; American Chemical Society: Washington, DC, 1995; ORGN 023.

(2) (a) Dittmer, D. C.; Discordia, R. P.; Zhang, Y.; Murphy, C. K.; Kumar, A.; Pepito, A. S.; Wang, Y. *J. Org. Chem.* **1993**, *58*, 718−731. (b) Kumar, A.; Dittmer, D. C. *J. Org. Chem.* **1994**, *59*, 4760−4764. (c) Pepito, A.; Dittmer, D. C. *J. Org. Chem.* **1994**, *59*, 4311−4312. (d) Dittmer, D. C.; Zhang, Y.; Discordia, R. P. *J. Org. Chem.* **1994**, *59*, 1004−1010. (e) Discordia, R. P.; Dittmer, D. C. *J. Org. Chem.* **1990**, *55*, 1414−1415. (f) Discordia, R. P.; Murphy, C. K.; Dittmer, D. C. *Tetrahedron Lett.* **1990**, *31*, 5603−5606. (g) Polson, G.; Dittmer, D. C. *Tetrahedron Lett.* **1986**, *27*, 5579−5582. (h) Kumar, A.; Dittmer, D. C. *Tetrahedron Lett.* **1994**, *35*, 5583−5586.

(3) Suggested by Dr. Douglas Livingstone.

(4) Lewis, R. J., Sr. *Sax's Dangerous Properties of Industrial Materials*; Van Nostrand Reinhold: New York, 1996; Vol. III, TAJ 500, p 3068. (b) Sittig, M. *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, 2nd ed.; Noyes: Park Ridge, NJ, 1985; pp 828−829. (c) Cooper, W. C. *Tellurium*; Van Nostrand Reinhold: New York, 1971; pp 313−321. (d) Elemental tellurium has been removed from the Superfund list since it does not meet the criteria for hazardous substances: *Chem. Eng. News* **1994**, Oct 17, 38.

(5) (a) Wang, Y.; Dittmer, D. C. *Abstracts of Papers,* 211th National Meeting of the American Chemical Society, New Orleans, LA, Mar 24−28, 1996; American Chemical Society: Washington, DC, 1996; ORGN 430. (b) Xu, Q.; Chao, B.; Wang, Y.; Dittmer, D. C. *Tetrahedron* **1997**, *53*, 12131−12146.

(6) Chao, B.; McNulty, K. C.; Dittmer, D. C. *Tetrahedron Lett.* **1995**, *36*, 7209−7212.

(7) Colored solutions of $(Te)_n^{2-}$ are often obtained in the reduction of tellurium.

(8) (a) Gonda, J.; Helland, A.-C.; Ernst, B.; Bellus, D. *Synthesis* **1993**, 729−733. (b) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301−6311. (c) Alcón, M.; Canas, M.; Poch, M.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron Lett.* **1994**, *35*, 1589−1592. (d) Burgess, K.; Liu, L. T.; Pal, B. *J. Org. Chem.* **1993**, *58*, 4758−4763. (e) For recent examples of conversions of N-activated aziridines by ring-opening to substituted *β*- and α-amino acids see: Davis, F. A.; Reddy, G. V.; Liang, C.-H. *Tetrahedron Lett.* **1997**, *38*, 5139−5142. Davis, F. A.; Liang, C.-H.; Liu, H. *J. Org. Chem.* **1997**, *62*, 3796−3797.

(9) (a) Reviewed by Cheikh, R. B.; Chaabouni, R.; Laurent, A.; Mison, P.; Nafti, A. *Synthesis* **1983**, 685−700. (b) For a general discussion about amine synthesis that includes allylic amines and reactions of aziridines, see: Mitsunobu, O. In *Comprehensive Organic Synthesis*; Trost, B., Ed.; Pergamon: Oxford, 1991; Vol. 6, pp 65−101. (c) A brief summary of methods is given in the introduction to a paper describing the synthesis of allylic amines by borohydride reduction of imines: DeKimpe, N.; Stanoeva, E.; Verhe, R.; Schamp, N. *Synthesis* **1988**, 587−592.

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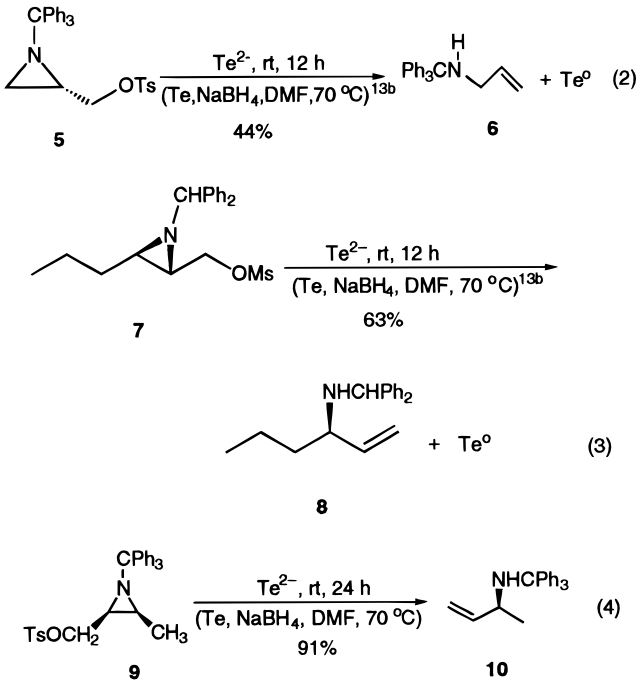
Results and Discussion

While nucleophilic ring opening of epoxides can occur smoothly without overt activation by a Brønsted or Lewis acid (eq 1),[11] that of aziridines is sluggish unless the nitrogen functionality is converted into a better leaving group by attachment of an electron-withdrawing, activating group (e.g., $-SO_2R$, $-COR$) or by protonation.[10x,12] Apparently, telluride is so powerful a nucleophile that it does not require activation of an aziridinemethanol sulfonate. The nucleophilic reduction of eq 1 is successful with aziridines **5**, **7**, and **9** in which the nitrogen is substituted with a trityl or a benzhydryl group (eqs 2−4).



Yields have not been optimized. The products **8**[8c] and **10** from optically active **7** and **9**, respectively, also are optically active. The lack of activation of **5**, **7**, and **9** may be more apparent than real since the borane−trimethylamine byproduct that we identified previously in the borohydride−DMF reduction medium[2b] may be playing a role as a Lewis acid,[2a,d] although the bulky N-substituent would be expected to shield the nitrogen atom from complexation. X-ray analysis of **10** showed a large trityl−N−C bond angle of 118.7° also seen, although not as extreme, in *N*-*tert*-butylamines.[13a] It was not possible to prepare the tosylate of *trans*-*N*-trityl-3-phenyl-2-aziridinemethanol, the *N*-trityl analogue of **11**, possibly because the trityl group sterically encumbers the hydroxymethyl group. Models show that the phenyl and trityl groups interfere with each other least when they are on opposite sides of the plane of the ring, i.e., when the trityl and hydroxymethyl groups are on the same side.

Activated aziridines **11** and **12** present three sites for attack by telluride ion, two aziridine ring carbon atoms, and the external carbon atom of the tosylate or mesylate. Mixtures were obtained in the telluride process, the components of which were not identified except for the α,β-unsaturated amino acid, **13**, an analogue of the

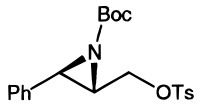
(10) Some articles of which the references may be consulted for earlier work follow. Displacements by nitrogen nucleophiles on allylic alcohol derivatives or of α-aminoalkyl cuprates on vinyl triflates: (a) Sen, S. E.; Roach, S. L. *Synthesis* **1995**, 756−758. (b) Dieter, R. K.; Dieter, J. W.; Alexander, C. W.; Bhinderwala, N. S. *J. Org. Chem.* **1996**, *61*, 2930−2931. Reaction of nitrogen nucleophiles with π-allylpalladium or iron derivatives: (c) Flegelova, Z.; Patek, M. *J. Org. Chem.* **1996**, *61*, 6735−6739. (d) Williams, J. M. J. *Synlett* **1996**, 705−710. (e) Pyne, S. G.; Dong, Z. *J. Org. Chem.* **1996**, *61*, 5517−5522. (f) Larock, R. C.; Tu, C. *Tetrahedron* **1995**, *51*, 6635−6650. (g) Besson, L.; Goré, J.; Cazes, B. *Tetrahedron Lett.* **1995**, *36*, 3857−3860. (h) Hutchins, R. O.; Wei, J.; Rao, S. J. *J. Org. Chem.* **1994**, *59*, 4007−4009. (i) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089−4090. (j) von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573−584. (k) Enders, D.; Finkam, M. *Synlett* **1993**, 401−402. (l) Hayashi, T.; Kishi, K.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 1743−1746. Allylic aminations: (m) Johannsen, M.; Jørgensen, K. A. *J. Org. Chem.* **1994**, *59*, 214−216. (n) Srivastava, R. S.; Nicholas, K. M. *Chem. Commun.* **1996**, 2335−2336. Reaction of alkynes with metalloimines, of titanium−alkyne derivatives with imines, or of propargylamines with aryl bromides via cross-coupling involving tri-*n*-butyltin hydride and palladium: (o) Génisson, Y.; Massardier, C.; Gautier-Luneau, I.; Greene, A. E. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2869−2872. (p) Takai, K.; Odaka, H.; Kataoka, Y.; Utimoto, K. *Tetrahedron Lett.* **1994**, *35*, 1893−1896. (q) Gao, Y.; Harada, K.; Sato, F. *Tetrahedron Lett.* **1995**, 5913−5916. (r) Corriu, R. J. P.; Bolin, G.; Moreau, J. J. E. *Bull. Soc. Chim. Fr.* **1993**, *130*, 273−280. Methylenation reactions (e.g., Wittig): see also ref 8a,d. (s) Rotella, D. P. *J. Am. Chem. Soc.* **1996**, *118*, 12246−12247. (t) Katritzky, A. R.; Hong, Q.; Chen, J.; Yang, Z.; Belyakov, S. A. *An. Quim. Int. Ed.* **1996**, *92*, 138−140; *Chem. Abstr.* **1996**, *125*, 275770. (u) Albeck, A.; Persky, R. *J. Org. Chem.* **1994**, *59*, 653−657. (v) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1991**, *56*, 1027−1036. (w) Wei, Z.-Y.; Knaus, E. E. *Synthesis* **1994**, 1463−1466. From aziridines: (x) Loreto, M. A.; Tardella, P. A.; Tofani, D. *Tetrahedron Lett.* **1995**, *36*, 8295−8298. (y) DeKimpe, N.; Jolie, R.; DeSmaele, D. *J. Chem. Soc., Chem. Commun.* **1994**, 1221−1222. (z) da Zhang, Z.; Scheffold, R. *Helv. Chim. Acta* **1993**, *76*, 2602−2615. Sigmatropic rearrangements: (aa) Overman, L. E.; Zipp, G. G. *J. Org. Chem.* **1997**, *62*, 2288−2291. (bb) Honda, K.; Tabuchi, M.; Inoue, S. *Chem. Lett.* **1996**, 385−386. (cc) Nishibayashi, Y.; Srivastava, S. K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **1995**, *36*, 6725−6728. (dd) Kurose, N.; Takahashi, T.; Koizumi, T. *J. Org. Chem.* **1996**, *61*, 2932−2933. (ee) Ichikawa, Y.; Tsuboi, K.; Isobe, M. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2791−2796. (ff) Imogai, H.; Petit, Y.; Larcheveque, M. *Tetrahedron Lett.* **1996**, *37*, 2573−2576. (gg) Shea, R. G.; Fitzner, J. N.; Fankhauser, J. E.; Spaltenstein, A.; Carpino, P. A.; Peevey, R. M.; Pratt, D. V.; Tenge, B. J.; Hopkins, P. B. *J. Org. Chem.* **1986**, *51*, 5243−5252. (hh) Brunko, M.; Khuong, T.-A. V.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 454−456. (ii) Whitesell, J. K.; Yaser, H. K. *J. Am. Chem. Soc.* **1991**, *113*, 3526−3529. (jj) Villemin, D.; Hachemi, M. *Synth. Commun.* **1996**, *26*, 1329−1334. (kk) Doherty, A. M.; Kornberg, B. E.; Reily, M. D. *J. Org. Chem.* **1993**, *58*, 795−798. Reduction of vinyl imines, allylic hydroxylamines, and allylic nitrones: see ref 9c. (ll) Hicks, F. A.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 2713−2718. (mm) Shia, W. S.; Lee, K.; Oh D. Y. *Tetrahedron Lett.* **1995**, *36*, 281−282. (nn) Braun, H.; Schmidtchen, F. P.; Schneider, A.; Simon, H. *Tetrahedron* **1991**, *47*, 3329−3334. (oo) Dondoni, A.; Merchán, F. C.; Merino, P.; Tejero, T. *Synth. Commun.* **1994**, *24*, 2551−2555. (pp) Bartoli, G.; Marcantoni, E.; Petrini, M. *J. Chem. Soc., Chem. Commun.* **1991**, 793−794. Addition of vinylmetal reagents to imines: (qq) Merino, P.; Anoro, S.; Castillo, E.; Merchan, F.; Tejero, T. *Tetrahedron: Asymmetry* **1996**, *7*, 1887−1890. (rr) Jones, C. A.; Jones, I. G.; North, M.; Pool, C. R. *Tetrahedron Lett.* **1995**, *36*, 7885−7888. (ss) Enders, D.; Schankat, J. *Helv. Chim. Acta* **1993**, *76*, 402−406. Elimination reactions of amines: see ref 8c. (tt) Breuilles, P.; Kaspar, K.; Uguen, D. *Tetrahedron Lett.* **1995**, *36*, 8011−8014. Reaction of allylic silanes with *N*-[(*p*-toluenesulfonyl)-imino]phenyliodinane: (uu) Kim, D. Y.; Choi, J. S.; Rhie, D. Y.; Chang, S. K.; Kim, I. K. *Synth. Commun.* **1997**, *27*, 2753−2760. Additions of ammonia to dienes: (vv) Kojima, R.; Yamashita, T.; Tanabe, K.; Shiragami, T.; Yasuda, M.: Shima, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 217−222.

(11) Lewars, E. G. In *Comprehensive Heterocyclic Chemistry*; Lwowski, W., Ed.; Pergamon: Oxford, 1984; Vol. 7, pp 108−113.

(12) (a) Ham, G. E. *J. Org. Chem.* **1964**, *29*, 3052−3055. (b) Padwa, A.; Woolhouse, A. D. In *Comprehensive Heterocyclic Chemistry*; Lwowski, W., Ed.; Pergamon: Oxford, 1984; Vol. 7, pp 70−72. (c) Tanner, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 599−619. (d) Tanner, D.; Gautun, O. R. *Tetrahedron* **1995**, *51*, 8279−8288. (e) Church, N. J.; Young, D. W. *Tetrahedron Lett.* **1995**, *36*, 151−154. (f) Ibuka, T.; Nakai, K.; Habashita, H.; Hotta, Y.; Otaka, A.; Tamamura, H.; Fujii, N.; Mimura, N.; Miwa, Y.; Taga, T.; Chounan, Y.; Yamamoto, Y. *J. Org. Chem.* **1995**, *60*, 2044−2058. (g) For example, a nonactivating *N*-trityl group of an aziridine 2-carboxylate ester had to be removed and replaced by a *p*-nitrobenzoyl group before a synthesis of unsaturated amino acids involving ring opening could proceed: Baldwin, J. E.; Adlington, R. M.; Robinson, N. G. *J. Chem. Soc., Chem. Commun.* **1987**, 153−155.

(13) (a) A *t*-Bu-N−CH_2 angle of 115.9° is reported by: Beale, J. P.; Grainger, C. T. *Cryst. Struct. Commun.* **1972**, *1*, 71−72. (b) Chen, J.; Zhou, X.-J. *Synthesis* **1987**, 586−587.

N-(benzyloxycarbonyl) methyl ester previously obtained by isomerization of a vinylglycine derivative.[14a] Phase-transfer catalysis gave the best yield of **13**, probably formed by the aforementioned isomerization (eq 5). The stereochemistry of **13** is believed to be *Z* by comparison with the ^{1}H NMR spectrum of the known (*Z*)-methyl ester.[14b]



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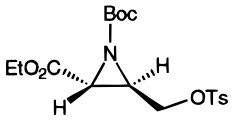

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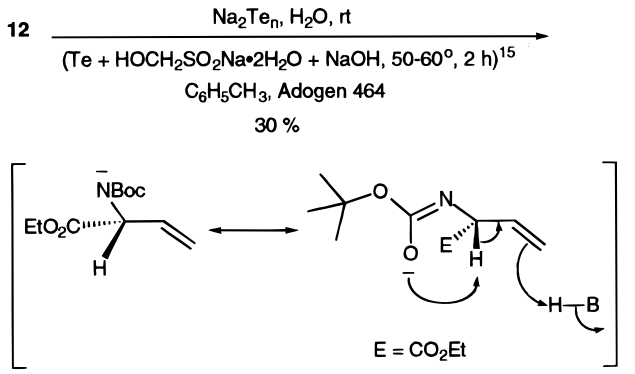
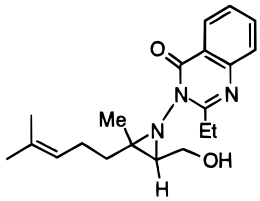


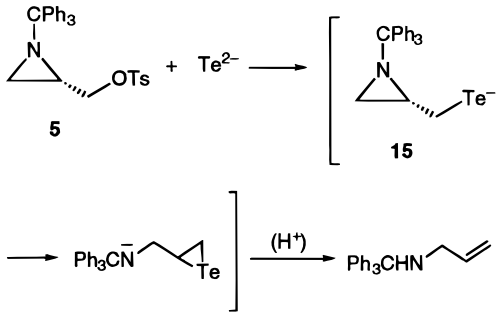
13

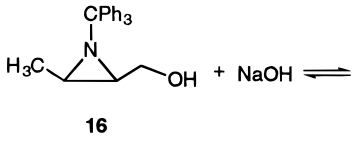
A bulky group, however, was a detriment to investigations of the *trans*-aziridinemethanol sulfonate ester of **14**. When such a group adopts a cisoid configuration with respect to the hydroxymethyl group, the latter is shielded from reaction with *p*-toluenesulfonyl chloride or methanesulfonyl chloride. In aziridinemethanols such as **14**,[16] the large substituent on the nitrogen atom is expected to adopt a transoid configuration with respect to the larger of the two substituents on the carbon atoms of the aziridine ring.[17] In **14**, the hydroxymethyl group is the least bulky and, therefore, is protected from reaction by the substituent on nitrogen. The aziridinemethanol **14** could not be converted to a sulfonate ester, and when treated with *p*-toluenesulfonyl chloride−triethylamine−DMAP, it gave an unknown compound or compounds possibly related to the known elimination reaction of the quinazolinone group on nitrogen.[18]



14

The powerfully nucleophilic telluride in **15** (eq 6) is able to effect opening of the unactivated aziridine ring exemplified in compounds **5**, **7**, and **9**, which contrasts with the stability of *N*-tritylaziridinemethanol **16** (eq 7) in an attempted aza-Payne rearrangement.[12f] The *N*-Boc analogue of **16**, an activated aziridine, "yielded a complex mixture of products under the same conditions", and the N-tosyl analogue gave a 30:70 mixture of aziridinemethanol and the *N*-tosyloxiranemethanamine (the product of the aza-Payne rearrangement).[12f]





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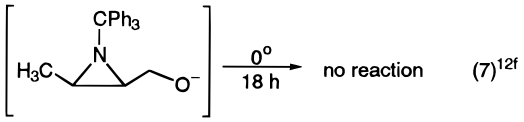

The telluride reaction with aziridines is limited, as present observations demonstrate, to substrates in which a reactive substituent on the nitrogen atom does not interfere with derivatization of the alcohol function and in which electron-withdrawing substituents on nitrogen are absent. The increasing availability of aziridines (especially of enantiomerically enriched examples),[18,19] the mild reaction conditions, and the recovery and reuse of tellurium commend the method as a useful addition to the ways in which allylic amines can be prepared. Preparations of allylic amines from aziridines, in addition to those previously reviewed,[9a] involve addition of ethoxycarbonylnitrene to allylsilanes (some in high enantiomeric purity) to give unstable aziridines that eliminate the silyl group with concomitant ring opening and double

(14) (a) Afzali-Ardakani, A.; Rapoport, H. *J. Org. Chem.* **1980**, *45*, 4817−4820. (b) Zhu, Y.-F.; Yamazaki, T.; Tsang, J. W.; Lok, S.; Goodman, M. *J. Org. Chem.* **1992**, *57*, 1074−1081.

(15) Tschugaeff, L.; Chlopin, W. *Chem. Ber.* **1914**, *47*, 1269−1275.

(16) Atkinson, R. S.; Kelly, B. J. *J. Chem. Soc., Chem. Commun.* **1988**, 624−625.

(17) (a) Texier, F.; Carrié, R. *Bull. Soc. Chim. Fr.* **1971**, 4119−4128. (b) Ahman, J.; Somfai, P. *J. Am. Chem. Soc.* **1994**, *116*, 9781−9782. (c) Only the anti isomer of the *N*-tritylimine of propionaldehyde is formed, demonstrating the preference of the trityl group for a syn proton over a syn ethyl group: Sasai, H.; Arai, S.; Tahara, Y.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 6656−6657. (d) Also, we were not able to prepare a mesylate or tosylate derivative of *trans*-3-phenyl-1-tritylaziridinemethanol, possibly because the bulky trityl group blocks the reaction with the alcohol function.

(18) Atkinson, R. S.; Coogan, M. P.; Lochrie, I. S. T. *J. Chem. Soc., Chem. Commun.* **1996**, 789−790.

bond formation[10x,20] and a number of free-radical-based transformations.[10y,z,21]

Experimental Section

Reagents were obtained from commercial sources and were used without purification unless specified otherwise. Thin-layer chromatography was done on silica gel (250 μm) and visualized by ultraviolet light, I_2, phosphomolybdic acid, or anisaldehyde. Flash column chromatography was done with silica gel/60 (240−400 mesh).[22] Tetrahydrofuran (THF) was distilled from Na−Ph_2CO. Methylene chloride was distilled from CaH_2, and *N*,*N*-dimethylformamide (DMF) was purified by treatment with KOH pellets for 4 h followed by distillation under reduced pressure from BaO or CaO. Methanol was degassed by passage of a stream of argon for at least 30 min. Triethylamine and pyridine were distilled prior to use. All reactions were done in oven-dried glassware. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ unless otherwise specified. *J* values are given in Hz. Optical rotations were obtained by use of a 1-mL quartz cell with a path length of 10 cm. Capillary gas chromatography was performed with columns of either a cross-linked methylsilicone gum, a 5% phenyl methyl silicone ultrahigh performance, or a cross-linked methyl silicone-fused silica. Sharpless asymmetric epoxidations were performed as described previously.[23] Melting points are uncorrected. Elemental Te was reduced according to previously published procedures.[2a,13b,15] All reactions involving Te were done under Ar or N_2. X-ray analytical data for **10**[34] (Supporting Information) was obtained on a Siemens SMART CCD system (SHELXTL solutions package).

1-(Triphenylmethyl)-2-aziridinemethanol *p*-Toluenesulfonate (5). 1-(Triphenylmethyl)-2-aziridinemethanol[24] (0.50 g, 1.68 mmol) was treated with NEt_3 (0.28 mL, 1.98 mmol), 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (4.0 mg, 0.03 mmol), and tosyl chloride (0.33 g, 1.7 mmol) in CH_2Cl_2 to give **5** as white crystals (0.630 g, 1.34 mmol, 84.8%): mp 53−55 °C; ^{1}H NMR δ 1.12 (d, 1 H, J = 6.0), 1.51−1.53 (m, 1 H), 1.70 (d, 1 H, J = 2.8), 2.45 (s, 3 H), 4.13 (dd, 1 H, J = 10, 5.6), 4.29 (dd, 1 H, J = 10, 5.7), 7.17−7.44 (m, 17 H), 7.73 (d, 2 H, J = 8.2) [lit.[25] data for 1-*tert*-butyl-2-aziridinemethyl tosylate: ^{1}H NMR (60 MHz, CCl_4) δ 0.9 (s, 9 H), 1.3 (d, 1 H), 1.9 (m, 1 H), 2.4 (s, 3 H), 3.6−4.1 (m, 2 H), 7.1−7.8 (m, 4 H)]; ^{13}C NMR δ 21.6, 25.5, 30.6, 72.4, 73.8, 126.8, 127.5, 127.6, 127.9, 129.3, 129.4, 129.8, 143.9.

***N*-(Triphenylmethyl)allylamine (6).** Tellurium (0.11 g, 0.85 mmol) was reduced by $NaBH_4$ (68.7 mg, 1.79 mmol) in DMF.[2a,13b] Tosylate **5** (0.20 g, 0.42 mmol) in DMF (2.0 mL) was added, and precipitation of black Te was observed simultaneously. The reaction mixture was allowed to stir overnight and was worked up as previously described.[2a] The crude product was passed through a silica gel pipet column (1:2 Et_2O−hexanes) to give the known allylamine **6** as white crystals (55.5 mg, 0.18 mmol, 44%): R_f = 0.67 (1:2 Et_2O−hexanes); mp 82−84 °C (lit.[26] mp 85, 81, 84−85 °C); ^{1}H NMR δ 1.6 (br s, 1 H), 2.8 (d, 2 H, J = 5.5), 5.1 (dd, 1 H, J = 10.4, 1.3), 5.3 (m, 1 H), 5.9−6.0 (m, 1 H), 7.2−7.5 (m, 15 H); ^{13}C NMR δ 46.5, 70.7, 114.7, 126.2, 127.8, 128.6, 137.3, 146.1.

(2*S*,3*R*)-1-(Diphenylmethyl)-3-propyl-2-aziridinemethyl Methanesulfonate (7). The aziridine derivative was prepared from (2*S*,3*S*)-3-*n*-propyl-2-oxiranemethanol [2.00 g, 17.2 mmol, $[\alpha]^{24}_D$ −49.9 (*c* 1.10, $CHCl_3$)] according to the procedure described by Riera, Pericas, and co-workers[19i,27] based on earlier work by Sharpless and Caron.[28] The intermediate, (2*R*,3*R*)-3-(α-phenylbenzylamino)-1,2-hexanediol, was isolated as a thick, colorless liquid (2.77 g, 9.24 mmol, 53.7%, 90% pure by GC): $[\alpha]^{24}_D$ −24.2 (*c* 4.4, $CHCl_3$); ^{1}H NMR δ 0.9 (t, 3 H, J = 7.1), 1.2−1.6 (m , 5 H), 2.0−2.4 (br s, 2 H), 2.7 (m, 1 H), 3.6−3.7 (m, 3 H), 5.0 (s, 1 H), 7.2−7.4 (m, 10 H); ^{13}C NMR δ 14.2, 18.9, 32.5, 57.4, 64.2, 64.5, 71.4, 127.2, 127.4, 128.6, 143.8.

The amino diol (1.99 g, 6.64 mmol) in CH_2Cl_2 (6.6 mL) was treated at 0 °C with triethylamine (3.8 mL, 26.5 mmol) and methanesulfonic anhydride (3.01 g, 19.9 mmol) in CH_2Cl_2 (10 mL), the latter being added sequentially. The solution was stirred at 0 °C for 6 h and at room temperature for 24 h, the progress of the reaction being followed by TLC. Water (10 mL) was added, and the resulting solution was stirred for 30 min. Layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). Organic layers were combined, washed with brine, and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (1:2 Et_2O−hexanes) to yield aziridinemethanol mesylate **7** (0.98 g, 2.72 mmol, 41%) as a viscous liquid: $[\alpha]^{22.5}_D$ +67.4 (*c* 3.40, MeOH) [lit[19i] $[\alpha]^{23}_D$ +63.2 (*c* 1.4, MeOH)]; ^{1}H NMR δ 0.9 (t, 3 H, J = 7.2), 1.2−1.4 (m, 4 H), 1.8−1.9 (m, 1 H), 2.1−2.2 (m, 1 H), 2.7 (s, 3 H), 4.00 (dd, 1 H, J = 11, 7.3), 4.3 (dd, 1 H, J = 11, 5.3), 4.3 (s, 1 H), 7.2−7.5 (m, 10 H); ^{13}C NMR d 21.6, 27.8, 37.5, 42.2, 43.2, 69.2, 69.6, 71.7, 126.7, 127.7, 128.2, 142.7. The methanesulfonamide of α-phenylbenzenamine also was obtained (0.40 g, 1.54 mmol, 23%), presumably formed by mesylation of the benzhydrylamino group followed by displacement of Ph_2CHNH-SO_2CH_3: mp 151−155 °C (lit.[29] mp 151−152 °C); ^{1}H NMR δ 2.6 (s, 3 H), 5.3−5.4 (d, 1 H, J = 7.5), 5.7−5.8 (d, 1 H, J = 7.6), 7.3−7.4 (m, 10 H).

***N*-[1(*R*)-Ethenylbutyl]-α-phenylbenzenemethanamine (8).** The procedure followed is described above for allylic amine **6**. Treatment of aziridinemethanol mesylate **7** (0.95 g, 2.66 mmol) with tellurium (0.68 g, 5.33 mmol) and $NaBH_4$ (0.33 g, 7.99 mmol) in DMF (20 mL) yielded the known allylic amine **8**[8c] as a yellow oil after purification by flash

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column chromatography (1:2 Et_2O/hexanes on recycled silica gel) (0.440 g, 1.69 mmol, 63%): $[\alpha]^{23}_D$ −8.2 (*c* 1.73, $CHCl_3$); ^1H NMR δ 0.9 (t, 3 H, J = 6.9), 1.5−1.6 (m, 5 H), 2.9−3.0 (m, 1 H), 5.0 (s and d, 2 H, overlapping peaks), 5.2 (dd, 1 H, J = 10.2, 1.8), 5.6−5.7 (m, 1 H), 7.2−7.5 (m, 10 H); ^{13}C NMR δ 14.1, 19.1, 38.3, 58.5, 63.5, 115.6, 126.8, 127.3, 127.5, 128.3, 141.2.

(2*S*,3*S*)-1-(Triphenylmethyl)-3-methyl-2-aziridinecarboxylic Acid Methyl Ester.[12e,30] A procedure reported for the 2*R*,3*R* isomer was followed.[31] The 2*S*,3*S* ester was purified by trituration with hexanes and recrystallization from MeOH: mp 101−102 °C [lit.[30a] mp 103−107 °C]; $[\alpha]^{24}_D$ −98.6 (*c* 1.04, $CHCl_3$) [lit. for 2*R*,3*R* isomer[31] $[\alpha]^{20}_D$ +98 (*c* 1.04, $CHCl_3$); $[\alpha]^{23}_D$ for 2*S*,3*S* isomer[30a] −79.7 (*c* 1.1, THF)]; ^1H NMR δ 1.4 (d, 3 H, J = 5.4), 1.6−1.7 (m, 1 H), 1.9 (d, 1 H, J = 6.4), 3.7 (s, 3 H), 7.2−7.5 (m, 15 H); ^{13}C NMR δ 13.3, 34.8, 35.9, 51.8, 75.0, 126.8, 127.6, 129.3, 143.9, 170.7.

(2*S*,3*S*)-1-(Triphenylmethyl)-3-methyl-2-aziridinemethanol.[19b] The reduction of (2*S*,3*S*)-1-(triphenylmethyl)-3-methyl-2-aziridinecarboxylic acid methyl ester was done according to a procedure described by Deyrup and Moyer.[25] The ester (3.69 g, 10.3 mmol) was added to a suspension of $LiA1H_4$ (0.64 g, 19.2 mmol) in Et_2O (82 mL) and stirred for 3 h. The reaction was worked up by addition of H_2O (6.4 mL) and 15% aqueous NaOH (2.0 mL). The resulting suspension was filtered, the residue washed generously with Et_2O, and the solvent removed by evaporation. Crystallization of the aziridinemethanol was done with hexanes/CH_2Cl_2 (19:1) to yield white crystals (2.85 g, 8.66 mmol, 84.4%): mp 112−113 °C [lit.[19b] mp 86−88 °C; lit.[19c] 110−112 °C]; $[\alpha]^{23}_D$ +16.7 (*c* 1.02, $CHCl_3$) [lit.[19b] $[\alpha]_D$ +16.5 (*c* 1.06, $CHCl_3$)]; IR (KBr) 3430 (br), 1480 (s), 1438 (s), 1058 (m), 1024 (s) cm^{-1}; ^1H NMR δ 1.3 (d, 3 H, J = 6.0), 1.4 (m, 1 H), 1.8 (m, 1 H), 3.7−3.9 (m, 2 H), 7.2−7.6 (m, 15 H) [lit.[19b] ^1H NMR ($CDCl_3$) δ 1.3 (m, 3 H), 1.4 (m, 1 H), 1.7 (m, 1 H), 3.8 (m, 2 H), 7.1−7.5 (m, 15 H)]; ^{13}C NMR δ 13.5, 30.9, 36.2, 61.2, 74.5, 126.7, 127.5, 129.3, 144.6.

(2*S*,3*S*)-1-(Triphenylmethyl)-3-methyl-2-aziridinemethyl *p*-Toluenesulfonate (9). The aziridinemethanol above (0.502 g, 1.52 mmol) was treated with NEt_3 (0.265 mL, 1.90 mmol), 4-DMAP (3.71 mg, 0.03 mmol), and tosyl chloride (0.32 g, 1.67 mmol) in CH_2Cl_2 (ca. 15 mL) to give **9** as colorless crystals (0.72 g, 1.48 mmol, 97.4%) after recrystallization from CH_2Cl_2−MeOH: mp 149.5−151 °C; $[\alpha]^{23}_D$ −40.5 (*c* 1.05, $CHCl_3$); ^1H NMR δ 1.2 (d, 3 H, J = 5.4), 1.2 (m, 1 H), 1.4 (m, 1 H), 2.4 (s, 3 H), 4.1 (dd, 1 H, J = 10.2, 7.45), 4.4 (dd,1 H, J = 10, 5.2), 7.2−7.5 (m, 17 H), 7.7 (d, 2 H, J = 8.2); ^{13}C NMR δ 13.4, 21.6, 30.9, 32.9, 69.7, 74.4, 126.7, 127.5, 127.8, 129.2, 129.8, 133.1, 144.2, 144.7. Anal. Calcd for $C_{30}H_{29}O_3NS$: C, 74.50; H, 6.04; N, 2.90. Found: C, 74.36; H, 6.05; N, 2.84.

(2*S*)-*N*-(Triphenylmethyl)-3-buten-2-amine (10). Tellurium (0.26 g, 2.07 mmol) was reduced by $NaBH_4$ (0.19 g, 5.00 mmol) in DMF (8.0 mL) as described in the general procedure. Tosylate **9** (0.50 g, 1.04 mmol) in DMF (2.0 mL) was added and the mixture stirred for 24 h. The crude product was passed through a plug of silica gel with elution by hexanes to give allylamine **10** as a clear, viscous liquid (0.28 g, 0.94 mmol, 91.1%) that was crystallized from MeOH: mp 61−62 °C; $[\alpha]^{23.5}_D$ −33.7 (*c* 1.04, $CHCl_3$); ^1H NMR δ 0.6 (d, 3 H, J = 6.6), 1.3 (d, 1 H, J = 2.1), 3.1 (m, 1 H), 4.8 (d, 1 H, J = 10), 5.0 (d, 1 H, J = 17), 5.6 (ddd, 1 H, J = 17, 10, 6.1), 7.1−7.7 (m, 15 H); ^{13}C NMR δ 23.0, 51.0, 71.5, 111.6, 126.2, 127.7, 128.9, 144.2, 147.1. Anal. Calcd for $C_{23}H_{23}N$: C, 88.13; H, 7.40; N, 4.47. Found: C, 88.08; H, 7.39; N, 4.41.

(2*R,3*R**)-1-(*tert*-Butyloxycarbonyl)-3-phenyl-2-aziridinemethanol *p*-Toluenesulfonate (11).** The *N*-Boc-aziridinemethanol was prepared according to a procedure described by Ziegler and Belema.[19f] The analogous *cis*-3-[4-(methylthio)phenyl]aziridinemethanol has been described recently.[32] (2*S*,3*S*)-3-Phenyloxiranemethanol[23a] (5.78 g, 38.5 mmol) in CH_2Cl_2 (150 mL) was treated with imidazole (3.17 g, 46.2 mmol), TBDMSCl (8.79 g, 58.3 mmol), and 4-DMAP (236 mg, 1.92 mmol) to give crude silyl ether as a thick, yellow oil (8.31 g, 31.4 mmol, 82%): $[\alpha]^{21.5}_D$ −29.7 (*c* 1.08, $CHCl_3$); ^1H NMR δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.9 (s, 9 H), 3.1 (m, 1 H), 3.8 (overlapping signals, 2 H), 3.9 (dd, 1 H, J = 12.0, 3.0), 7.3−7.4 (m, 5 H); ^{13}C NMR δ −5.3, 18.4, 25.9, 55.9, 62.8, 63.0, 125.7, 128.1, 128.4, 137.2.

A solution of the silyl ether (1.01 g, 3.83 mmol) in MeOH (10.0 mL) was heated to reflux with NaN_3 (0.760 g, 11.5 mmol), NH_4Cl (0.309 g, 5.75 mmol), and H_2O (1.60 mL) to yield a mixture of isomeric azido alcohols with one isomer predominating, presumably the 3-azido-3-phenyl derivative (1.11 g, 3.63 mmol, 94%): $[\alpha]^{22}_D$ −98.3 (*c* 1.02, $CHC1_3$); ^1H NMR δ 0.078 (s, 3 H), 0.09 (s, 3 H), 0.91 (s, 9 H), 2.5 (br s, 1 H, OH), 3.6−3.8 (m, 2 H), 3.8 (br d, 1 H, J = 3.6), 4.6 (d, 1 H, J = 7.1), 7.3 (m, 5 H); ^{13}C NMR δ −5.5, −5.4, 18.3, 25.8, 63.2, 66.6, 73.7, 127.8, 128.5, 128.7, 136.3; HRMS (FAB) *m/z* calcd for $C_{15}H_{26}N_3O_2Si(MH^+)$ 308.1794, found 308.1791.

The mixture of azido alcohols (1.11 g, 3.62 mmol) in toluene (5.00 mL) was treated with PPh_3 (1.03 g, 3.90 mmol) in toluene (10.0 mL) to yield the aziridine, purified by column chromatography (1:9 EtOAc−hexanes, then 1:4 EtOAc−hexanes), as a yellow oil (0.732 g, 2.78 mmol, 85%): $[\alpha]^{24}_D$ +49.0 (*c* 1.02, $CHCl_3$); ^1H NMR δ 0.09 (s, 3 H), 0.10 (s, 3 H), 0.9 (s, 9 H), 1.8 (br s, 1 H), 2.2 (br s, 1 H) 2.9 (d, 1 H, J = 2.3), 3.9 (d, 2 H, J = 1.9), 7.3 (m, 5 H); ^{13}C NMR δ −5.4, 18.3, 25.9, 42.2, 61.4, 125.8, 126.8, 128.3, 140.1; HRMS (FAB) *m/z* calcd for $C_{15}H_{26}NOSi$ (MH^+) 264.1784; found 264.1777.

The aziridine (0.217 g, 0.824 mmol) was converted to the *N*-Boc derivative by treatment with $(Boc)_2O$ (0.463 g, 2.06 mmol) in CH_2Cl_2 (4.0 mL) and a catalytic amount of 4-DMAP (30.5 mg, 0.247 mmol). The crude product was purified by column chromatography (0−5% EtOAc−hexanes) to yield the *N*-Boc aziridine silyl ether as a thick liquid (0.256 g, 0.705 mmol, 86%): $[\alpha]^{22}_D$ −48.8 (*c* 1.04, $CHCl_3$); ^1H NMR δ 0.09 (s, 3 H), 0.1 (s, 3 H), 0.9 (s, 9 H), 1.4 (s, 9 H), 2.8 (m, 1 H), 3.5 (d, 1 H, J = 3.1), 3.9 (dd, 1 H, J = 11.5, 3.7), 4.0 (dd, 1 H, J = 11.6, 3.3), 7.3 (m, 5 H); ^{13}C NMR δ −5.2, 18.2, 25.9, 28.0, 41.6, 46.6, 60.4, 81.0, 126.8, 127.7, 128.4, 136.6, 157.0; HRMS (FAB) *m/z* calcd for $C_{20}H_{33}NNaO_3Si$ (MNa^+) 386.2127, found 386.2119.

The *N*-Boc-aziridine silyl ether (0.774 g, 60% GC purity, 1.28 mmol) was dissolved in THF (4.0 mL) and treated with tetra-*n*-butylammonium fluoride in THF (2.43 mL, 1.0 M in THF, 2.43 mmol) to yield the aziridinemethanol, purified by column chromatography (1:4 EtOAc−hexanes) (0.299 g, 1.26 mmol, 99%): ^1H NMR δ 1.3 (s, 9 H), 2.8 (dd, 1 H, J = 9.1, 4.3) 2.9 (m, 1 H), 3.4 (d, 1 H, J = 3.1), 3.6 (m, 1 H), 4.1 (m, 1 H), 7.3−7.4 (m, 5 H); ^{13}C NMR δ 27.9, 42.0, 47.0, 62.0, 82.0, 126.6, 127.9, 128.4, 128.5, 161.0. The proton NMR spectrum is comparable to that for the known *N*-(*p*-toluenesulfonyl) derivative:[19b] δ 4.3, 4.2 (each ddd, CH_2O) 4.0 (d, J = 4.4, C_3−H), 3.1 (ddd, C_2−H). The general procedure for tosylation was followed. Aziridinemethanol (0.299 g, 1.26 mmol) in CH_2Cl_2 (1.50 mL) was treated with Ts_2O (0.496 g, 1.46 mmol) and 4-DMAP (3.10 mg, 0.0243 mmol). The tosylate **11** was purified by column chromatography (0−20% EtOAc−hexanes) and isolated as a white powder (0.260 g, 0.643 mmol, 52%): mp 82−83 °C; ^1H NMR δ 1.3 (s, 9 H), 2.4 (s, 3 H), 3.00 (m, 1 H), 3.4 (d, 1 H, J = 3.0), 4.1 (dd, 1 H, J = 11.2, 5.6), 4.4 (dd, 1 H, J = 11.2, 4.7), 7.2 (m, 2 H), 7.3 (m, 5 H), 7.8 (d, 2 H, J = 8.2); ^{13}C NMR δ 21.6, 27.7, 41.3, 44.0, 68.4, 81.9, 127.1, 128.0, 128.3, 128.4, 128.5, 129.9, 130.0, 145.1, 158.4.

The tosylate was treated with telluride ion (tellurium, rongalite, 1.0 N aqueous NaOH) under phase-transfer conditions [Adogen 464 (1 drop), distilled water (0.5 mL), toluene (2.5 mL)]. The reaction was stirred with a magnetic stirrer for 1 week. A mixture of unidentified compounds was obtained.

***p*-Toluenesulfonate Ester (12) of Ethyl (2*S*,3*S*)-1-(*tert*-Butyloxycarbonyl)-α-hydroxy-2-aziridinemethane-3-carboxylate.** The *tert*-butyldimethylsilyl ether of ethyl (2*S*,3*S*)-1-(*tert*-butyloxycarbonyl)-α-hydroxyaziridinemethane-3-carboxylate was prepared in the same way as the 2*R*,3*R* methyl ester.[19f] Ethyl (2*R*,3*S*)-α-hydroxyoxiranemethane-2-carboxy-

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late[33] (2.91 g, 19.9 mmol) yielded the aziridinemethanol as a yellow liquid (1.94 g, 7.49 mmol, 53%): $[\alpha]^{21.5}_D + 46.4$ (*c* 1.02, $CHCl_3$); ^{1}H NMR δ 0.08 (s, 6 H), 0.8 (s, 9 H), 1.3 (t, 3 H, J = 7.1), 1.7 (br s, 1 H), 2.4 (br s, 2 H), 3.6 (br m, 2 H), 4.2 (m, 2 H) [lit.[19f] (*R*,*R*)-methyl ester: ^{1}H NMR δ 0.05 (s, 6 H), 0.9 (s, 9 H), 1.3 (br s, 1 H), 2.4 (br s, 2 H) 3.7−3.5 (m, 2 H), 3.7 (s, 3 H)]; ^{13}C NMR δ −5.3, 14.1, 18.3, 25.8, 33.5, 40.0, 61.5, 64.7, 172.5 [lit.[19f] (*R*,*R*)-methyl ester: δ −5.5; 18.2, 25.7, 33.0, 39.8, 52.1, 64.3, 172.5].

A solution of the aziridinemethanol (1.75 g, 6.75 mmol), $(Boc)_2O$ (4.42 g, 19.6 mmol), and 4-DMAP (0.250 g, 2.02 mmol) yielded the *N*-Boc-aziridine as a thick, yellow liquid (2.08 g, 5.79 mmol, 86%): $[\alpha]^{21}_D$ −18.9 (*c* 1.23, $CHCl_3$); ^{1}H NMR δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.3 (t, 3 H, J = 7.1), 1.4 (s, 9 H), 2.9 (m, 1 H), 3.0 (d, 1 H, J = 2.5), 3.7 (dd, 1 H, J = 11.6, 4.2), 3.8 (dd, 1 H, J = 11.6, 3.8), 4.1−4.3 (m, 2 H) [lit.[19f] (*R*,*R*)-methyl ester: ^{1}H NMR δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.87 (s, 9 H), 1.4 (s, 9 H), 2.9 (m, 1 H), 3.0 (d, 1 H, J = 2.5), 3.7 (dd, 1 H, J = 11.6, 4.0), 3.8 (s, 3 H), 3.9 (dd, 1H, J = 11.6, 3.8)]: ^{13}C NMR δ −5.3, 14.2, 18.3, 25.8, 28.0, 38.0, 44.2, 61.2, 61.6, 81.7, 158.5, 168.3 [lit.[19f] (*R*,*R*)-methyl ester: δ −5.3, 18.4, 25.9, 28.0, 37.8, 44.3, 52.5, 61.0, 81.7, 158.4, 168.8].

The silyl protecting group was removed from the *N*-Boc silyl ether (1.90 g, 5.28 mmol) as described previously[19f] to give the *N*-Boc-aziridinemethanol derivative (1.00 g, 4.09 mmol, 77%) as an oil: $[\alpha]^{22}_D$ −3.8 (*c* 0.99, $CHCl_3$); ^{1}H NMR δ 1.3 (t, 3 H, J = 7.2), 1.4 (s, 9 H), 3.0 (m, 1 H), 3.1 (d, 1 H, J = 2.7), 3.7 (dd, 1 H, J = 12.4, 4.3), 3.9 (dd, 1 H, J = 12.4, 2.9), 4.2 (q, 2 H, J = 7.3) [lit.[19f] (*R*,*R*)-methyl ester: ^{1}H NMR δ 1.4 (s, 9 H), 1.9 (t, 1 H, J = 6.6, OH), 3.0 (m, 1 H), 3.1 (d, 1 H, J = 3.1), 3.7 (ddd, 1 H, J = 12.3, 7.3, 4.3), 3.8 (s, 3 H), 4.0 (ddd, 1 H, J = 12.3, 6.1, 2.8)]; ^{13}C NMR δ 14.1, 27.8, 37.6, 43.7, 60.2, 61.8, 82.3, 158.9, 167.9 [lit.[19f] (*R*,*R*)-methyl ester: δ 27.7, 37.4, 43.8, 52.4, 59.9, 82.1, 158.8, 168.4].

Tosylation of the *N*-Boc-aziridinemethanol (0.940 g, 3.83 mmol) was accomplished by treatment with Ts_2O (97%, 1.57 g, 4.60 mmol), NEt_3 (0.667 mL, 4.79 mmol), and 4-DMAP (11.0 mg, 0.077 mmol) in CH_2Cl_2 (5.00 mL). The crude product was purified by flash chromatography (20−50% Et_2O−hexanes) to yield the tosylate as a viscous, yellow-green liquid (1.20 g, 3.00 mmol, 78%): ^{1}H NMR δ 1.3 (t, 3 H, J = 7.2), 1.4 (s, 9 H), 2.4 (s, 3 H), 2.9 (d, 1 H, J = 2.3), 3.0 (m, 1 H), 3.9 (dd, 1 H, J = 11.2, 5.9), 4.1−4.3 (m, 3 H), 7.3 (d, 2 H, J = 8.1), 7.7 (d, 2 H, J = 8.2); ^{13}C NMR δ 14.1, 21.6, 27.8, 32.0, 39.9, 62.0, 68.0, 82.4, 128.0, 129.9, 132.4, 145.2, 157.6, 166.9.

Reaction of 12 with Telluride Ion. Tellurium (19.4 mg, 1.51 mmol) was reduced by rongalite (0.466 g, 3.00 mmol) and 1.0 N aqueous NaOH solution (3.00 mL, 3.00 mmol). After the solution cooled to room temperature, Adogen 464 (2 drops) in distilled water (1.0 mL) was added to the mixture, followed by a solution of aziridinyl tosylate **12** (20.7 mg, 0.52 mmol) in toluene (7.5 mL). The reaction was stirred vigorously with a magnetic stirrer for 18 h. Three new spots on TLC were observed. When the stirring was stopped, two layers were visible: the bottom layer was black, with black elemental Te being visible, and the top layer was yellow. The crude product mixture obtained from the toluene layer was purified by flash chromatography (0−15% EtOAc−hexanes) to yield the rearranged vinylglycine derivative **13** (34.0 mg, 0.149 mmol, 30%): ^{1}H NMR δ 1.3 (t, 3 H, J = 7.2), 1.5 (s, 9 H), 1.8 (d, 3 H, J = 7.2), 4.2 (q, 2 H, J = 7.2), 6.0 (br s, 1H), 6.7 (q, 1H, J = 7.2); [lit.[14b] (*Z*)-methyl ester: δ 1.5 (s, 9 H), 1.8 (d, 3 H, J = 8.0), 3.8 (s, 3 H), 6.2 (br, 1 H), 6.7 (q, 1 H, J = 8.0)]; ^{13}C NMR δ 14.4, 28.2 (overlapping CH_3 absorptions), 61.2, 80.3, 126.9, 131.4, 153.1, 164.8; HRMS (FAB) *m*/*z* calcd for $C_{11}H_{19}NNaO_4(MNa^+)$ 252.1212; found 252.1212. Two other products were not identified.

Quinazolinylaziridinemethanol 14. The aziridinemethanol was prepared from geraniol as reported by Atkinson and Kelly:[16] mp 126−130 °C [lit.[16] mp 128−130 °C]; IR (KBr pellet) 3446 (s), 1648 (s), 1589 (s), 1463 (m), 1353 (m), 1032 (s), 779 (s) cm^{-1}; ^{1}H NMR δ 1.4 (t, 3 H, J = 7.3), 1.45 (s, 3 H), 1.54 (s, 3 H), 1.6 (s, 3 H), 1.7 (m, 2 H), 2.0 (m, 1 H), 2.1−2.2 (m, 1 H), 2.7−2.8 (m, 1 H), 3.0 (dd, 1 H, J = 9.2, 3.0), 3.1 (m, 1 H), 3.7 (m, 1 H), 4.1 (m, 1 H), 4.5 (br d, 1 H, J = 4.5), 4.9 (t, 1 H, J = 6.6), 7.4 (t, 1 H, J = 7.2), 7.6−7.8 (m, 2 H), 8.2 (d, 1 H, J = 8.0); ^{13}C NMR δ 10.9, 17.2, 17.8, 25.4, 25.6, 27.7, 34.6, 54.4, 54.7, 61.6, 121.0, 122.2, 126.2, 126.3, 126.9, 133.1, 133.8, 146.0, 157.8, 161.0.

Treatment of **14** with TsCl (0.201 g, 1.05 mmol), NEt_3 (1.80 mL, 1.10 mmol), and 4-DMAP (2.17 mg, 0.018 mmol) in CH_2Cl_2 (5 mL) for 5 d at 0−4 °C resulted in decomposition of the starting material to unknown compounds. No tosylate ester was observed by IR and NMR spectroscopy.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds **5**, **11**, **12**, **13**, and **14** and for intermediates that have no combustion analysis are provided. HRMS data are included for **13**, the 1-TBDMS ether of 3-azido-4-phenyl-1,2-propanediol, and the TBDMS ether of 3-phenyl-2-aziridinemethanol and its *N*-Boc derivative. X-ray analytical data for **10** are provided (70 pages).[34] This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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