Iodocyclization of the (Tolylsulfonyl)- and (Trichloroacetyl)carbamates of Secondary α-Allenic Alcohols. Highly Diastereoselective Synthesis of *syn*-1,2-Amino Alcohols and *trans*-5-Alkyl-1-oxo-2-oxazolidine-4-carboxylic Acids

Richard W. Friesen* and Aleksandra E. Kolaczewska

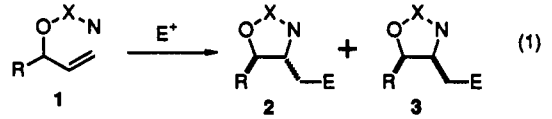
Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, Canada M5S 1A1

Received December 12, 1990 (Revised Manuscript Received May 1, 1991)

The iodocyclization of tosyl- and (trichloroacetyl)carbamates **9** and **10**, respectively, of secondary α-allenic alcohols is described. The cyclofunctionalization reactions are highly diastereoselective, providing *trans*-5-alkyl-4-(1-iodoethylene)-2-oxazolidinones **11** and **12** as the major diastereomers in ratios of 6.3:1 to >99:<1. The mechanism of cyclization involves the initial formation of diiodides resulting from the addition of I_2 to the terminal olefin of the allene moiety, followed by a kinetically controlled intramolecular S_N2' displacement of iodide. Hydrolysis and acetylation of the *N*-tosyloxazolidinones **11** provide *syn*-1,2-amino alcohol derivatives **15**. Alternatively, ozonolysis of the vinyl iodides derived from the cyclization of the (trichloroacetyl)carbamates **12** provides a novel, efficient, and highly diastereoselective route to *trans*-5-alkyl-2-oxazolidinone-4-carboxylic acids **25** and esters **26**.

Introduction

The electrophile-induced nucleophilic addition reactions of allylic alcohols and their derivatives have been the subject of much interest in recent years and have become a well-established synthetic method for introducing 1,2-asymmetry into cyclic and acyclic systems.[1-6] For those acyclic cases in which a nitrogen nucleophile is tethered through the oxygen atom, as in **1**, electrophilic cyclization provides, regiospecifically in many cases, the diastereomeric 1,2-amino alcohol derivatives **2** and/or **3** (eq 1).[1b]

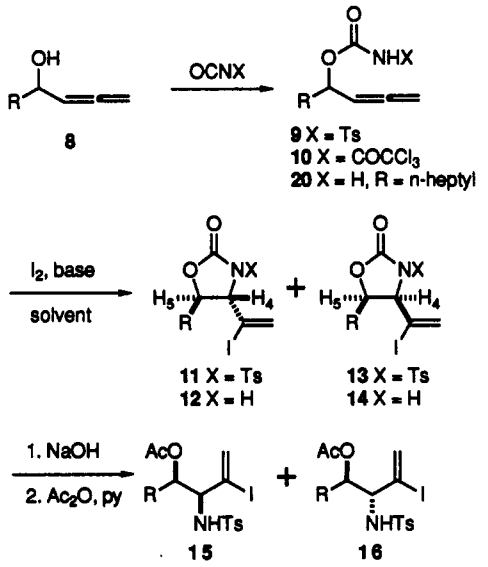


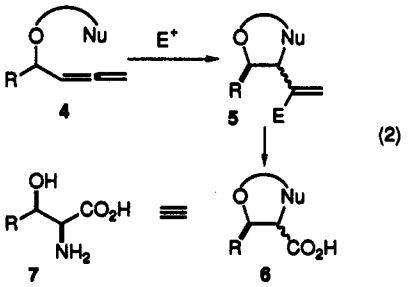
(1)

Such reactions have been performed on the imidate,[2] (*N*-acylamino)methyl ether,[3] thiocarbamidate,[5] and sulfonylcarbamate[6] derivatives of allylic alcohols and mechanistic models[7] have been proposed in an attempt to rationalize the observed diastereoselectivity of the addition process.

Several of these methods have been utilized with great success in the synthesis of various types of biologically active acyclic polyfunctionalized compounds containing 1,2-amino alcohols.[8-12] Our interest in the preparation of such systems led us to consider the corresponding intramolecular cyclization reactions of α-allenic alcohol derivatives **4** (eq 2), which, prior to our initial report,[13] had not been described.[14] This latter process would appear to be

Scheme I





(2)

(1) (a) For two excellent reviews on this subject, see: (a) Cardillo, G.; Orena, M.; Sandri, S. *Pure Appl. Chem.* **1988**, *60*, 1679. (b) Cardillo, G.; Orena, M. *Tetrahedron* **1990**, *46*, 3321. (b) For examples of the intramolecular electrophilic addition reactions of other allylic alcohol and allylic amine systems, see refs 1a and 7.

(2) (a) Cardillo, G.; Orena, M.; Sandri, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1489. (b) Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *J. Org. Chem.* **1986**, *51*, 4905.

(3) Harding, K. E.; Stephens, R.; Hollingsworth, D. R. *Tetrahedron Lett.* **1984**, *25*, 4631.

(4) Hegedus, L. S.; Mulhern, T. A.; Asada, H. *J. Am. Chem. Soc.* **1986**, *108*, 6224.

(5) Knapp, S.; Patel, D. V. *J. Am. Chem. Soc.* **1983**, *105*, 6985.

(6) Hirama, M.; Iwashita, M.; Yamazaki, Y.; Ito, S. *Tetrahedron Lett.* **1984**, *25*, 4963.

(7) Chamberlin, A. R.; Mulholland, R. L.; Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 672 and references cited therein.

(8) See, for example: Sakaitani, M.; Ohfune, Y. *J. Am. Chem. Soc.* **1990**, *112*, 1150 and references cited therein.

(9) (a) Echinocandins: Benz, F.; Nuesch, J.; Treichler, H.; Voser, W.; Nyfeler, R.; Keller-Schierlein, W. *Helv. Chim. Acta* **1974**, *57*, 2459. (b) Cyclosporine: Shioiri, T.; Hamada, Y. *Heterocycles* **1988**, *27*, 1035. (c) OF4949-I and II: Sano, S.; Ikai, K.; Katayama, K.; Takesako, K.; Nakamura, T.; Obayashi, A.; Ezure, Y.; Enomoto, H. *J. Antibiot.* **1986**, *39*, 1685.

(10) Miller, M. J. *Acc. Chem. Res.* **1986**, *19*, 49.

(11) For some leading references and recent examples of the preparation of α-amino-β-hydroxy acids, see: (a) Jung, M. E.; Jung, Y. H. *Tetrahedron Lett.* **1989**, *30*, 6637. (b) Roemmele, R.; Rapoport, H. *J. Org. Chem.* **1989**, *54*, 1866.

(12) Takahata, H.; Banba, Y.; Tajima, M.; Momose, T. *J. Org. Chem.* **1991**, *56*, 240 and references cited therein.

(13) Friesen, R. W. *Tetrahedron Lett.* **1990**, *30*, 4249.

0022-3263/91/1956-4888$02.50/0

Table I. Iodocyclization of the Tosyl- and (Trichloroacetyl)carbamates of Secondary α-Allenic Alcohols

entry	substrate	conditions[a]	ratio 11:13 or 12:14[b,c]	coupling constant $J_{4,5}$(Hz)[c] trans, cis	isolated 15 or 12[d]	yield, %
1	9a, R = c-hexyl	A	7.2:1	2.7, 6.6	15a/16a	33[e]
2		B	6.6:1		15a/16a	35[e]
3		C	15:1		15a/16a	38[e]
4		D	40:1		15a	74
5		E	29:1		15a/16a	68[e]
6		F	12:1		15a/16a	52[e]
7	9b, R = *n*-heptyl	A	1.1:1	3.3, 7.3	15b/16b	62[e]
8		D	21:1		15b	74
9	9c, R = isobutyl	A	1:1	3.3, 7.4	15c/16c	49[e]
10		D	27:1		15c	77
11	9d, R = isopropyl	A	8.8:1	3.0, 6.9	15d/16d	47[e]
12		D	30:1		15d	76
13	9e, R = *tert*-butyl	A	>99:<1	3.1	15e	18
14		D	>99:<1		15e	59
15	9f, R = phenyl	D[f]	10:1[g]	2.9, 6.7	15f/16f	50[e]
16	8b, R = *n*-heptyl	G	6.3:1	4.5, 7.8	12b	69
17	8a, R = c-hexyl	G	>99:<1	4.1	12a	65
18	8d, R = isopropyl	G	>99:<1	4.4	12d	71
19	8e, R = *tert*-butyl	G	>99:<1	4.2	12e	38
20	8f, R = phenyl	G	>99:<1	5.1	12f	73

[a] Reaction conditions: I_2 (2 equiv); A, aqueous $NaHCO_3$, Et_2O, rt; B, aqueous $NaHCO_3$, THF, rt; C, aqueous $NaHCO_3$, CCl_4, rt; D, K_2CO_3, Et_2O, rt; E, K_2CO_3, Et_2O, 0 °C; F, K_2CO_3, CCl_4, rt; G, $OCNCOCCl_3$, Et_2O, rt; I_2 (2 equiv), K_2CO_3, Et_2O, rt (one pot, see text). [b] Measured from the integrated ^1H NMR spectra of the crude reaction mixtures (estimated error ≤2%). [c] The minor isomers in entries 13, 14, and 17–20 could not be detected by ^1H NMR spectroscopy. [d] Isolated yield of analytically pure product. [e] Isolated yield of a homogeneous mixture. Analytically pure samples of the major and minor isomers were also obtained (see Experimental Section). [f] Carbamate not isolated. [g] Ratio measured from spectrum of 15f/16f.

an attractive one since potentially synthetically versatile substituted olefin **5** was anticipated to be formed as the reaction product. When viewed with respect to the synthesis of **6** for example, ozonolysis of a vinyl halide **5** (E = halide) would be expected[15] to provide the corresponding acid or ester.

Herein, we describe the full details of (1) the novel, efficient, and highly trans diastereoselective intramolecular iodoamination reactions of the (tolylsulfonyl)-[13] and (trichloroacetyl)carbamates **4** (Nu = CONHR) of secondary α-allenic alcohols and (2) the preparation of *trans*-5-alkyl-1-oxo-2-oxazolidine-4-carboxylic acids by the ozonolysis of the resulting vinyl iodides **5** (E = I).

Results and Discussion

Iodocyclization. Our initial efforts focused on the cyclization reactions of the tosylcarbamates **9a–f** (Scheme I). These materials were easily prepared in isolated yields of >85% from the corresponding α-allenic alcohols **8a–f**[16] by treatment with tosyl isocyanate in CH_2Cl_2 at room temperature.[17] Our early experiments utilized the carbamate **9a** and involved variation of the iodocarbamation reaction conditions (Table I, entries 1–6). Examination of the integrated ^1H NMR spectra of the crude reaction mixtures, obtained by treating **9a** with I_2 and base for 24 h, indicated the presence of two predominant products corresponding to the diastereomeric trans (major) and cis (minor) cyclic urethanes **11a** and **13a**, respectively (vide infra). The observed ratios of **11a** and **13a** are listed in Table I. Unfortunately, these carbamates could not be efficiently separated from one another or from other minor reaction products by column chromatography. However, conversion of the carbamates into the acyclic 1,2-acetoxy-*N*-tosylamines **15a** and **16a** by hydrolysis (NaOH, aqueous MeOH) and acetylation (Ac_2O, py, DMAP) provided chromatographically pure mixtures of **15a** and **16a** that could also be analyzed by ^1H NMR spectroscopy. The ratios obtained in this manner were the same as the ratios that were measured in the spectra of the crude reaction mixtures of the cyclic carbamates. Although the isomers **15a** and **16a** were isolated from this reaction sequence as mixtures in order to obtain accurate ratio measurements, the major and/or minor isomers could also be isolated as pure compounds by column chromatography.

The three-step sequence was applied to a variety of tosylcarbamates **9b–f**, utilizing two of the iodocyclization reaction conditions, in order to demonstrate the generality of the overall process and to study the effect of the R substituent on the cyclization diastereoselectivity. These results are summarized in Table I, entries 7–15. Reaction sequences in which the initial cyclizations were performed in anhydrous ether (condition D in Table I) were higher yielding and more diastereoselective than those carried out in aqueous solvent mixtures (condition A in Table I). In all cases, one oxazolidinone diastereomer (and thus, one acyclic amino alcohol diastereomer) predominated and its relative proportion was found to increase in the series from R = *n*-heptyl (21:1) to R = *tert*-butyl (>99:<1).

It was imperative at this point that we unambiguously assign the relative stereochemistry of the carbamate cyclization products. ^1H NMR spectroscopy has been used to make this stereochemical assignment in related oxazolidinone systems. For example, $J_{4,5cis}$ and $J_{4,5trans}$ are observed to be 7.5 Hz and 4.5 Hz, respectively, in the ^1H NMR spectra of 4-alkyl-5-(iodomethyl)-2-oxazolidinones **17**.[18] However, in the spectra of 4-alkyl-5-vinyl-2-oxazo-

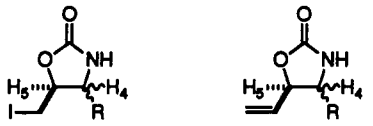
(14) The related cyclizations of γ-allenic alcohols and amines (to form 2-alkenyltetrahydrofurans and -pyrrolidines) have been studied. (a) Chilot, J.-J.; Doutheau, S.; Gore, J. *Bull. Soc. Chim. Fr.* **1984**, 307. (b) Walkup, R. D.; Park, G. *J. Am. Chem. Soc.* **1990**, *112*, 1597. (c) Arseniyadis, S.; Gore, J. *Tetrahedron Lett.* **1983**, *24*, 3997. (d) Kinsman, R.; Lathbury, D.; Vernon, P.; Gallagher, T. *J. Chem. Soc., Chem. Commun.* **1987**, 243. (e) For a general review of the electrophilic addition reactions of allenic materials, see: Smadja, W. *Chem. Rev.* **1983**, *83*, 263.

(15) Griesbaum, K.; Keul, H. *Angew. Chemie, Int. Ed. Engl.* **1975**, *14*, 716. These authors obtained methyl esters from the ozonolysis of vinyl chlorides in methanol.

(16) Prepared according to Cowie, J. S.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 720.

(17) The alcohols **8** could be stored at −5 °C for several weeks with little decomposition but they rapidly decomposed when stored at room temperature. The corresponding tosylcarbamates **9** exhibited similar stability.

(18) (a) Cardillo, G.; Orena, M.; Sandri, S. *J. Org. Chem.* **1986**, *51*, 713. (b) Foglia, T. A.; Swern, D. *J. Org. Chem.* **1969**, *34*, 1680.



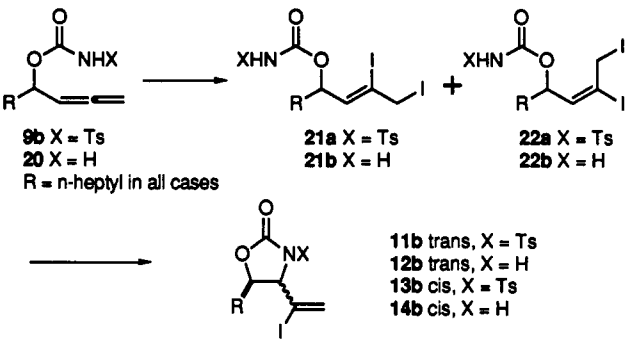
17 18

lidinones **18**, while this trend is also observed ($J_{4,5trans} < J_{4,5cis}$), the difference between the observed values is much smaller. Indeed, $J_{4,5cis} = J_{4,5trans} = 7$ Hz in 4-isobutyl-5-vinyl-2-oxazolidinone **18** (R = isobutyl).[19] In all of our compounds, the value of $J_{4,5}$ for the major cyclic carbamates (2.7 to 3.3 Hz) is observed to be smaller than the corresponding value for the minor isomers (6.6 to 7.4 Hz) (see Table I). While these observations allowed us to tentatively assign the major isomers (exhibiting the smaller $J_{4,5}$ values) as the trans carbamates **11a–f**, the assignment was tenuous, based on the values observed for the 4-alkyl-5-vinyl-2-oxazolidinones **18**. Our stereochemical assignment was confirmed by an X-ray crystallographic study of the major acyclic *N*-tosylamino alcohol derivative obtained from the reactions shown in Table I, entries 1–6.[20] This analysis demonstrated that the major product of the reaction sequence was indeed the syn amino alcohol **15a**, which arose from the trans cyclic carbamate **11a**. The other major products of the reaction sequences were thus assigned as the syn isomers **15b–f**, resulting from an initial trans diastereoselective iodocyclization reaction. It should be noted at this point that the iodocyclization reaction diastereoselectivity is greater and *opposite* to that observed in the analogous reactions of the tosylcarbamates of allylic alcohols (eq 1).[6]

It was felt that the synthetic utility of the iodocyclization reaction would be enhanced by the utilization of carbamates containing a nitrogen protecting group that could be more easily removed from carbamates such as **11** or **12** after an initial diastereoselective cyclization. Thus, we chose to look at the reactions of the (trichloroacetyl)carbamates **10** (Scheme I). When we attempted to prepare **10b** from the corresponding α-allenic alcohol **8b** by treatment with $OCNCOCCl_3$,[21] the trichloroacetyl group was hydrolyzed upon column chromatography and only the deacetylated carbamate **20** was isolated. As a result, we have developed a one-pot procedure in which the initially formed carbamates **10** are utilized directly in the iodocyclization reaction without isolation or purification (Scheme I). Our results are summarized in Table I, entries 16–20.

An ethereal solution of the appropriate α-allenic alcohol **8** was treated with a slight excess (1.1 equiv) of $OCNCOCCl_3$, followed by I_2/K_2CO_3 (2 equiv each), and the resulting mixture was stirred for 48–96 h at room temperature until TLC analysis indicated the disappearance of the initially formed product (vide infra). After workup, and in all cases except one, analysis of the ^1H NMR spectra of the crude reaction mixtures indicated the presence of a *single* 4,5-disubstituted, deacetylated oxazolidinone that was subsequently identified as the trans diastereomer **12** (vide infra). Only in the case of a primary R group was the isomeric cis carbamate **14b** observed (Table I, entry 16). In addition, a small amount (<10%) of the corresponding cyclic carbonates was observed in each case.

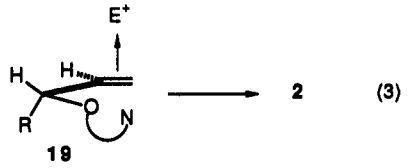
Scheme II



The crystalline oxazolidinones **12**, purified by column chromatography and recrystallization, were obtained in the isolated yields indicated in Table I. The coupling that is observed between the H4 and H5 protons in the ^1H NMR spectra of these compounds, although somewhat larger than those observed in the cyclic tosylcarbamates **11** ($J_{4,5}$ = 4.1–5.1 Hz for **12** compared to $J_{4,5trans}$ = 2.7–3.3 Hz for **11**; see Table I), suggests that they are also of the trans configuration.[22] Confirmation of this stereochemical assignment was again obtained by a single-crystal X-ray crystallographic analysis of the oxazolidinone **12b**.[20]

In general, the iodocyclization reactions of the (trichloroacetyl)carbamates **10** are simpler to perform (no isolation of the (trichloroacetyl)carbamate is necessary) and exhibit higher diastereoselectivity than the reactions of the corresponding tosylcarbamates **9**. In addition, these reactions provide pure trans oxazolidinones **12** directly without having to resort to subsequent synthetic operations to obtain separable materials. However, the reactions of both substrates provide the trans carbamates **11** or **12** in a highly diastereoselective manner and in synthetically useful yields.

Iodocyclization Mechanism. The mechanism that has been postulated to account for the trans diastereoselectivity that is observed in the cyclization of allylic alcohol derivatives (eq 3) involves a preferential attack of the



19

electrophile on one face of the olefin of a substrate conformer in which the allylic oxygen is in the plane of the double bond, as in **19**. The electrophile approaches the olefin from the face syn to the allylic hydrogen to yield a π complex that reacts with the internal nucleophile to provide, under kinetically controlled conditions, the trans heterocycle **2**.[7]

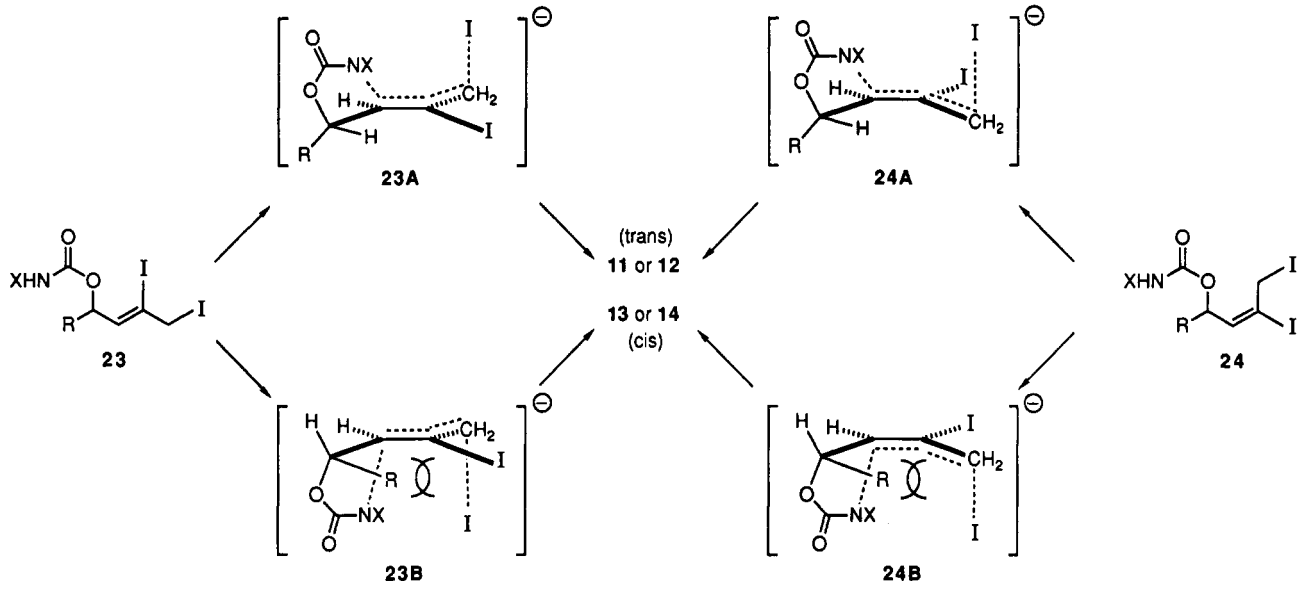
(19) The $J_{4,5}$ values observed by these authors (ref 8) vary only slightly from the cis (J = 6–8 Hz) to the trans (J = 6–7 Hz) isomers for a variety of R substituents in **18**.

(20) ORTEP representations and crystallographic data (bond lengths, bond angles, and torsion angles) are included in the supplementary material. Full details of the X-ray crystal structure will be reported elsewhere.

(21) Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109.

(22) An interesting observation was made in the proton-decoupled ^{13}C NMR spectra of a number of these oxazolidinone vinyl iodides and oxazolidinone carboxylic acids (vide infra). For those spectra recorded in aprotic solvents (acetone-d_6 and $CDCl_3$), several of the resonances were doubled (two singlets of similar resonant frequency), while, in protic solvent (CD_3OD), these same resonances were observed as single resonances. For example, in the spectrum of the trans oxazolidinone **12d** (100 MHz, acetone-d_6), the resonances attributed to the *C*HN, *C*I=C, and OCON carbons were observed at δ 63.9/64.0, 116.75/116.79, and 158.1/158.2 ppm, respectively. The same sample in CD_3OD exhibited single resonances for these same carbons at δ 64.9, 116.2, and 161.2 ppm. We attribute this observation to the existence of diastereomeric pairs of oxazolidinone dimers in aprotic solvents. In CD_3OD, the hydrogen bonding between the oxazolidinones that is responsible for the formation of the dimers in aprotic solvent is destroyed by preferential hydrogen bonding with the solvent.

Scheme III



In contrast to the proposed mechanism for the electrophilic cyclization reactions of allylic alcohol derivatives,[7] the mechanism of the iodocyclization reaction of the allenic analogues **9** and **10** may not involve trapping of an initially formed iodonium ion complex or intermediate. We suggest, based on a study of the reactions of **9b** and **20** (Scheme II), that the cyclization reactions of the α-allenic alcohol carbamates proceed by the initial formation of diiodides such as **21** and **22**,[23] followed by a kinetically controlled intramolecular S_N2' displacement to form the trans carbamates **11** and **12**.

Treatment of **9b** with I_2 and K_2CO_3 in dry ether provided, after 30 min, two new compounds that did not correspond to the cyclic carbamates **11b** or **13b**. Isolation of these somewhat unstable materials indicated that I_2 had added nonstereoselectively to the terminal double bond of the allene to provide an approximately equimolar mixture (71%) of the inseparable *Z* and *E* diiodides **21a** and **22a**, respectively, that were identified by suitable difference NOE experiments (Scheme II).[23] Similar treatment of carbamate **20** with I_2 and K_2CO_3 in dry ether also yielded, after 1 h, an approximate 1.5:1 mixture (59%) of the separable *Z* and *E* diiodides **21b** and **22b**, respectively.[24]

It is apparent that the initially formed materials in all of the cyclization reactions are the *Z* and *E* diiodides resulting from the addition of I_2 to the terminal olefin of the allene moiety. Yet to be established was the possibility for the direct conversion of these diiodides into the oxazolidinones by the intramolecular S_N2' displacement of iodide. Also of interest was the potential for the isomerization of the diiodides in the reaction mixture prior to cyclization.

An ethereal solution of the *E* diiodide **22b** was treated with I_2 in the absence of base in order to address this latter possibility. Under these conditions, **22b** readily isomerized to provide a 1:1.8 mixture of **21b**:**22b** after 4 h. It is possible that, in the presence of excess iodine, the diiodides undergo an isomerization process prior to cyclization and that cyclization proceeds solely from the one of the isomeric diiodides. However, there is evidence that the cyclized materials can arise directly from both diiodide isomers via an intramolecular S_N2' displacement.

Resubjection of the 1:1 diiodide mixture of **21a**/**22a** to the conditions of the original reaction, or, more importantly, treatment with K_2CO_3 alone in dry ether, provided crude reaction mixtures of **11b**/**13b** whose ^1H NMR spectra were identical with those observed previously (Table I, entry 7). Separate exposure of each of the diiodides **21b** and **22b** to the conditions of the original iodocyclization reaction (I_2, K_2CO_3, ether, 67 h), or exposure to NaH in THF at room temperature, provided, in each case, mixtures of the carbamates **12b**/**14b** in which the trans:cis ratio was >99:<1.[25] Thus, the favored production of the trans oxazolidinones **11** and **12** directly from the diiodides upon exposure to base alone indicates that the cyclized materials can arise from intramolecular S_N2' displacement and does not necessarily involve prior *Z*/*E* isomerization or the intermediacy of iodonium species.

Finally, the stereochemical outcome of the cyclization reaction is a result of kinetic control rather than a simple thermodynamic preference of the trans isomers **11** and **12** over the cis isomers **13** and **14**. Treatment of a 1:1 mixture of **11b** and **13b** (Table I, entry 6) with I_2 and K_2CO_3 in dry ether for 24 h did not alter the original trans:cis ratio. Similarly, treating the *N*-trichloroacetyl derivative of the pure minor carbamate **14b** with I_2 and K_2CO_3 in ether did not result in any observable cis to trans isomerization.

It follows that an explanation for the trans diastereoselectivity observed in all of the cyclization processes can be proposed upon inspection of the transition states involved in an intramolecular S_N2' displacement from either of the initially formed diiodides corresponding to **23** or **24** (Scheme III). It can be clearly seen that steric $A^{1,3}$ strain between the R substituent and either the vinyl I atom or

(23) The observation of diiodides resulting from the addition of I_2 to the terminal olefin of monosubstituted allenes[13] has recently been reported. Shaw, R.; Anderson, M.; Gallagher, T. *Synlett* **1990**, 584.

(24) The major *Z* diiodide **21b** is a stable, solid material that does not undergo appreciable decomposition if stored in the dark under argon, while the minor *E* diiodide **22b** readily isomerizes to a mixture of **21b**:**22b** when stored as a neat sample under the same conditions.

(25) The high trans diastereoselectivity of the cyclization reactions of the diiodides **21b** and **22b** is in contrast to the reaction in which the α-allenic alcohol **8b** was converted directly to the cyclic products **12b** and **14b** in a ratio of 6.3:1 (Table I, entry 16). The obvious difference in the cyclizations of the diiodides **21b** and **22b** compared to this latter reaction is the absence of the trichloroacetyl moiety on the carbamate nitrogen during the cyclization. It seems probable, then, that the trichloroacetyl moiety is still present on the carbamate nitrogen during the cyclization reactions of the (trichloroacetyl)carbamate **10b** and that deacetylation occurs in the reaction mixture only after cyclization.

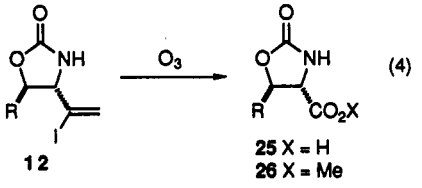
Table II. Ozonolysis of Oxazolidinone Vinyl Iodides

entry	substrate	product	yield, %
1	12a	25a	91
2	12b	25b	99
3	12b	26b	65
4	12d	25d	94
5	12e	25e	98
6	12f	25f	97
7	12f	26f	67

the CH_2I moiety in cyclization transition states **23B** and **24B**, respectively, would energetically disfavor formation of the cis oxazolidinones **13** or **14**.[26] Thus, the preferential formation of the trans isomers **11** or **12** stems from the absence of these steric interactions in cyclization transition states **23A** and **24A**.

Irrespective of the *E*/*Z* stereochemistry of the initially formed diiodides in either carbamate series, and irrespective of the actual mechanism of the iodocyclization reaction,[27] the favored mode of cyclization provides the trans cyclic carbamates **11** and **12** in a highly diastereoselective manner and in synthetically useful yields.

Ozonolysis of the Vinyl Iodide. In order to demonstrate the synthetic potential of the vinyl iodide produced in the iodocyclization reaction, we have prepared the 2-oxazolidinone derivatives of a number of *syn*-α-amino-β-hydroxy acids and esters (eq 4). Ozonolysis of the vinyl



(4)

iodides **12** in CH_2Cl_2 at −78 °C,[15] followed by the addition of aqueous KOH or NaOH, provided the corresponding acids **25**[28] in excellent yields (Table II). These 2-oxazolidinones can be isolated directly from the ozonolysis reaction mixture without an oxidative workup or chromatography. The observed value of $J_{4,5}$ (4.2–4.9 Hz) in each of these materials was consistent with the values reported for other *trans*-5-alkyl-1-oxo-2-oxazolidine-4-carboxylic acids,[8,29,30] indicating that no epimerization of the α-center had occurred during the basic workup. Alternatively, the methyl esters of these acids can be obtained directly by conducting the ozonolysis of the vinyl iodides in anhydrous MeOH at −78 °C.[15] This possibility is illustrated by the conversion of **12b,f** to the methyl esters **26b,f** (Table II, entries 3 and 7). However, in these latter cases, column chromatography is necessary to obtain pure materials and the yields are lower than for the formation of the parent acids.

Conclusions

We have demonstrated that the iodocyclization reactions of the tosyl- and (trichloroacetyl)carbamates of secondary α-allenic alcohols are highly diastereoselective, providing, in ratios ranging from 6.3:1 to >99:<1, the trans oxazolidinones **11** and **12**. The trans diastereoselectivity is the result of a kinetically controlled cyclization of the initially formed *Z* and *E* diiodides. The cyclic urethanes so produced can either be converted into *syn*-1,2-amino alcohol derivatives **15** (from the tosylcarbamates **11**) or isolated directly as the deacetylated trans oxazolidinones **12**. Simple ozonolysis of these latter materials provides a novel and straightforward access to useful derivatives of *syn*-α-amino-β-hydroxy acids **25** in very good overall yield from readily available α-allenic alcohols **8**. Further work is aimed at exploring the synthetic utility of these highly functionalized oxazolidinone vinyl iodides for the preparation of other acyclic polyfunctionalized materials containing the *syn*-1,2-amino alcohol moiety.

Experimental Section

General Procedures. ^1H NMR spectra were recorded at 200 MHz in $CDCl_3$, unless stated otherwise, using TMS or $CHCl_3$ as internal standard. Broad band proton-decoupled ^{13}C NMR spectra were recorded at 50 MHz in $CDCl_3$, using $CDCl_3$ as internal standard, unless stated otherwise. The underlined values in the ^{13}C NMR data refer to those resonances that are doubled but are due to a single carbon.[22] IR spectra were recorded on neat samples, unless stated otherwise. Solvents were anhydrous and transferred via syringes under an argon atmosphere. Workup procedures involving the drying of organics was done with $MgSO_4$. Distillation temperatures are air-bath temperatures in Kugelrohr distillation. Column chromatography was carried out on 230–400-mesh silica gel (40–63 μm), eluting with the solvents indicated. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.[31]

The secondary α-allenic alcohols **8** were prepared by the two-step procedure of Landor and co-workers[16] from the corresponding aldehydes and THP-protected propargyl alcohol in yields of 80–90%.[17]

1-Cyclohexyl-2,3-butadienol (8a): colorless liquid (distillation air-bath temperature, 100–110 °C/15 Torr); IR 3356, 2925, 2853, 1955, 1450, 1018, 841 cm^{-1}; ^1H NMR δ 0.9–1.9 (m, 12 H), 3.94 (tt, 1 H, *J* = 2.3, 6.6 Hz), 4.84 (dd, 2 H, *J* = 2.3, 6.6 Hz), 5.22 (q, 1 H, *J* = 6.6 Hz); ^{13}C NMR δ 25.78, 25.84, 26.2, 28.1, 28.4, 43.9, 74.1, 77.0, 93.1, 207.6; exact mass calcd for $C_{10}H_{16}O$ (M^+) 152.1202, found 152.1150.

1,2-Undecadien-4-ol (8b): colorless oil (distillation air-bath temperature, 115–120 °C/15 Torr); IR 3347, 2927, 2857, 1957, 1466, 1019, 842 cm^{-1}; ^1H NMR δ 0.88 (m, 3 H), 1.2–1.7 (m, 13 H), 4.18 (m, 1 H), 4.86 (dd, 2 H, *J* = 2.4, 6.6 Hz), 5.25 (q, 1 H, *J* = 6.6 Hz); ^{13}C NMR δ 13.8, 22.4, 25.2, 29.1, 31.6, 37.3, 69.7, 77.1, 94.8, 207.4; exact mass calcd for $C_{11}H_{20}O$ (M^+) 168.1515, found 168.1510.

6-Methyl-1,2-heptadien-4-ol (8c). This material was extremely volatile and was invariably contaminated with ether solvent. **8c**: colorless liquid (distillation air-bath temperature, 80–90 °C/15 Torr); IR 3338, 2958, 2928, 2871, 1956, 1469, 1367, 1060, 1013, 842 cm^{-1}; ^1H NMR δ 0.92 (d, 3 H, *J* = 6.6 Hz), 0.94 (d, 3 H, *J* = 6.6 Hz), 1.30–1.59 (m, 2 H), 1.69–2.00 (m, 2 H), 4.24 (m, 1 H), 4.84 (d, 1 H, *J* = 6.8 Hz), 4.86 (d, 1 H, *J* = 6.8 Hz), 5.23 (q, 1 H, *J* = 6.8 Hz); ^{13}C NMR δ 22.1, 22.8, 24.4, 46.4, 68.0, 77.2, 95.1, 207.4; exact mass calcd for $C_8H_{14}O$ (M^+) 126.1045, found 126.1035.

(26) The *A* values of I and CH_3 are reported to be 0.43 and 1.70, respectively. (Hirsch, J. A. In *Topics in Stereochemistry*, Volume 1; Allinger, N. L., Eliel, E. L., Eds.; John Wiley & Sons: New York, 1967; pp 199–222.) The R group would experience steric strain from the CH_2I moiety in **24B** similar to that of a CH_3 group since the departing I atom is required to be syn to the incoming nucleophile in an S_N2' process.

(27) It should be noted that the reactions described above do not necessarily rule out a mechanism analogous to that described above for the allylic alcohol derivatives involving an iodonium complex or intermediate on the internal double bond of the allene (similar to **19**). This type of species could potentially arise from the diiodides in the reaction mixture. The predicted stereochemical outcome of the reaction would nonetheless remain the same.

(28) It has been demonstrated that the 2-oxazolidinone derivatives of these acids **25** are useful for the determination of the relative configuration of the parent acid by ^1H NMR spectroscopy[29] and that they are easily converted, under nonepimerizing conditions, to the α-amino-β-hydroxy acid or ester.[30]

(29) Futagawa, S.; Inui, T.; Shiba, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3308.

(30) Acidic conditions: (a) Hirama, M.; Hiaki, H.; Ito, S. *Tetrahedron Lett.* **1988**, *25*, 3125. (b) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron* **1988**, *44*, 5253. Basic conditions on the derived *N*-BOC methyl esters: (c) Evans, D. A.; Weber, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 7151. (d) Ishizuka, T.; Kunieda, T. *Tetrahedron Lett.* **1987**, *28*, 4185.

(31) Compounds that were not characterized by combustion analysis were homogeneous by TLC analysis and gave satisfactory spectroscopic data indicative of their purity. ^1H NMR spectra for these compounds can be found in the supplementary material.

5-Methyl-1,2-hexadien-4-ol (8d). This material was extremely volatile and was invariably contaminated with ether solvent. **8d**: colorless liquid (distillation air-bath temperature, 80–100 °C/15 Torr); IR 3385, 2961, 2875, 1957, 1469, 1384, 1023, 843 cm^{-1}; ^1H NMR δ 0.93 (d, 3 H, J = 6.8 Hz), 0.96 (d, 3 H, J = 6.8 Hz), 1.77 (m, 1 H), 2.12 (br s, 1 H), 3.96 (m, 1 H), 4.85 (d, 1 H, J = 6.6 Hz), 4.87 (d, 1 H, J = 6.6 Hz), 5.22 (q, 1 H, J = 6.6 Hz); ^{13}C NMR δ 17.5, 17.8, 34.0, 74.6, 77.1, 92.9, 207.7; exact mass calcd for $C_7H_{13}O$ $(M + H)^+$ 113.0966, found 113.0930.

5,5-Dimethyl-1,2-hexadien-4-ol (8e). This material was extremely volatile and was invariably contaminated with ether solvent. **8e**: colorless liquid (distillation air-bath temperature, 120–130 °C/15 Torr); IR 3409, 2958, 2872, 1957, 1479, 1364, 1053, 1007, 841 cm^{-1}; ^1H NMR δ 0.93 (s, 9 H), 1.57 (br s, 1 H), 3.83 (m, 1 H), 4.86 (d, 1 H, J = 6.6 Hz), 4.87 (d, 1 H, J = 6.6 Hz), 5.28 (q, 1 H, J = 6.6 Hz); exact mass calcd for $C_8H_{15}O$ $(M + H)^+$ 127.1124, found 127.1132.

1-Phenyl-2,3-butadienol (8f): colorless oil (distillation air-bath temperature, 110–120 °C/15 Torr); IR 3358, 3062, 3030, 1955, 1494, 1453, 1193, 1024, 850, 700, 634 cm^{-1}; ^1H NMR δ 2.38 (br s, 1 H), 4.89 (d, 1 H, J = 6.4 Hz), 4.92 (d, 1 H, J = 6.4 Hz), 5.24 (m, 1 H), 5.42 (q, 1 H, J = 6.4 Hz), 7.37 (m, 5 H); ^{13}C NMR δ 71.9, 78.1, 95.2, 126.2, 127.9, 128.6, 143.0, 207.4; exact mass calcd for $C_{10}H_9O$ $(M - H)^+$ 145.0654, found 145.0657.

Preparation of Tosylcarbamates 9a–f. The procedure described below for the preparation of **9a** is typical. To a solution of the alcohol **8a** (307.7 mg, 2.02 mmol) in CH_2Cl_2 (5 mL) at room temperature was added tosyl isocyanate (0.46 mL, 1.1 equiv) dropwise. The resulting mixture was stirred at room temperature for 10 min. After an aqueous workup, involving the addition of water (20 mL) and extraction with CH_2Cl_2 (3 × 10 mL), drying, and concentration, the resulting semisolid was subjected to column chromatography (2:1 hexanes/ethyl acetate, v/v). The carbamate **9a**, a colorless, viscous oil (642.5 mg, 91%) that solidified at 5 °C, displayed the following physical properties: IR 3228, 2927, 2853, 1955, 1747, 1447, 1350, 1224, 1162, 1091, 852, 666 cm^{-1}; ^1H NMR δ 0.8–1.8 (m, 11 H), 2.45 (s, 3 H), 4.72 (m, 2 H), 4.93 (tt, 1 H, J = 1.5, 6.9 Hz), 5.02 (q, 1 H, J = 6.9 Hz), 7.53 (m, 2 H), 7.40 (br s, 1 H), 7.92 (m, 2 H); ^{13}C NMR δ 21.3, 25.4, 25.8, 27.7, 28.0, 41.4, 76.8, 79.2, 88.3, 128.3, 129.5, 135.8, 144.8, 150.5, 208.9; exact mass calcd for $C_{18}H_{23}NO_4S$ (M^+) 349.1349, found 349.1418.

Carbamate 9b: colorless, viscous oil (88%); IR 3247, 2928, 2861, 1958, 1748, 1446, 1351, 1224, 1163, 1091, 664 cm^{-1}; ^1H NMR δ 0.88 (br t, 3 H, J = 6.6 Hz), 1.22 (br, 10 H), 1.60 (br, 2 H), 2.45 (s, 3 H), 4.78 (m, 2 H), 5.04–5.16 (m, 2 H), 7.35 (m, 2 H), 7.40 (br s, 1 H), 7.93 (m, 2 H); ^{13}C NMR δ 13.9, 21.5, 22.4, 24.8, 28.9, 29.0, 31.6, 33.8, 75.3, 77.6, 90.1, 128.6, 129.7, 135.8, 145.2, 150.0, 208.8; exact mass calcd for $C_{19}H_{27}NO_4S$ (M^+) 365.1661, found 365.1666.

Carbamate 9c: colorless, viscous oil (99%); IR 3242, 2958, 2933, 2873, 1957, 1741, 1597, 1450, 1350, 1225, 1163, 1091, 772 cm^{-1}; ^1H NMR δ 0.85 (d, 6 H, J = 6.2 Hz), 1.37–1.63 (m, 3 H), 2.45 (s, 3 H), 4.77 (m, 2 H), 5.09 (q, 1 H, J = 6.5 Hz), 5.20 (m, 1 H), 7.35 (m, 2 H), 7.70 (br s, 1 H), 7.93 (m, 2 H); ^{13}C NMR δ 21.5, 22.0, 22.3, 24.2, 42.6, 73.9, 77.6, 90.2, 128.5, 129.7, 135.8, 145.1, 150.1, 208.8; exact mass calcd for $C_{16}H_{21}NO_4S$ (M^+) 323.1191, found 323.1142.

Carbamate 9d: colorless, viscous oil (85%); IR 3243, 2964, 2931, 2878, 1962, 1747, 1445, 1349, 1224, 1162, 1090, 666 cm^{-1}; ^1H NMR δ 0.85 (d, 3 H, J = 6.8 Hz), 0.87 (d, 3 H, J = 6.8 Hz), 1.87 (m, 1 H), 2.45 (s, 3 H), 4.63–4.80 (m, 2 H), 4.89–5.07 (m, 2 H), 7.34 (m, 2 H), 7.65 (br s, 1 H), 7.93 (m, 2 H); ^{13}C NMR δ 17.57, 17.60, 21.5, 32.0, 77.1, 79.8, 88.1, 128.5, 129.7, 135.8, 145.1, 150.1, 209.0; exact mass calcd for $C_{15}H_{19}NO_4S$ (M^+) 309.1035, found 309.1036.

Carbamate 9e: colorless, viscous oil (83%); IR 3246, 2965, 1959, 1747, 1598, 1445, 1350, 1229, 1163, 1091, 864, 665 cm^{-1}; ^1H NMR δ 0.87 (s, 9 H), 2.45 (s, 3 H), 4.57–4.75 (m, 2 H), 4.88 (dt, 1 H, J = 1.7, 7.3 Hz), 5.01 (dt, 1 H, J = 7.3, 6.4 Hz), 7.34 (m, 2 H), 7.90 (br s, 1 H), 7.92 (m, 2 H); ^{13}C NMR δ 21.5, 25.2, 34.9, 76.7, 82.4, 87.1, 128.3, 129.7, 135.9, 145.1, 150.2, 209.2; exact mass calcd for $C_{15}H_{18}NO_4S$ $(M - CH_3)^+$ 308.0957, found 308.0932.

Carbamate 9f. This material proved to be unstable to column chromatography and readily decomposed. Thus, typically this material was not isolated but, after workup, was immediately subjected to the iodocarbamation reaction. A small amount of **9f** was obtained as a partially pure sample (pale yellow foam) and exhibited the following physical properties: ^1H NMR δ 2.44 (s, 3 H), 4.81 (m, 2 H), 5.35 (q, 1 H, J = 6.6 Hz), 6.13 (dt, 1 H, J = 6.6, 2.3 Hz), 7.2–7.35 (m, 7 H), 7.37 (br s, 1 H), 7.90 (m, 2 H); ^{13}C NMR δ 21.5, 76.5, 78.2, 90.8, 127.0, 128.6, 128.7, 128.8, 129.7, 129.9, 135.6, 137.9, 145.2, 209.0; exact mass calcd for $C_{17}H_{25}NO_4SI$ $(M + H)^+$ 466.0550, found 466.0520.

Iodocyclization of Carbamates 9 (Condition D in Table I). The procedure described below for the preparation of **15b/16b** is typical. To a solution/suspension of the carbamate **9b** (221.0 mg, 0.6047 mmol) and solid K_2CO_3 (167 mg, 2 equiv) in dry ether (7 mL) was added solid I_2 (307 mg, 2 equiv), and the resulting mixture was stirred at room temperature overnight (15–24 h). Ethyl acetate (25 mL) was added followed by saturated, aqueous $Na_2S_2O_3$ (25 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 25 mL). The combined organics were dried and concentrated. The resulting crude reaction mixture was analyzed by ^1H NMR spectroscopy in order to determine the ratio of diastereomeric oxazolidinones **11b** and **13b** (Table I, entry 8). The crude mixture was dissolved in methanol (4 mL) and 10% aqueous NaOH (2 mL) and was stirred at room temperature for 15 h. The methanol was then removed, in vacuo and to the resulting mixture were added water (25 mL) and CH_2Cl_2 (25 mL). The aqueous phase was made slightly acidic (~pH 6) by the addition of 2% aqueous HCl and the organic layer was removed. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organics were dried and concentrated. The residual material was dissolved in pyridine (1 mL), and DMAP (7 mg, 0.06 mmol) and acetic anhydride (0.23 mL, 2.42 mmol) were added. After stirring at room temperature for 24 h, CH_2Cl_2 (25 mL) was added, and the solution was washed with saturated aqueous $CuSO_4$ (3 × 20 mL). The organic layer was dried and concentrated. Subjection of the residual material to column chromatography (4:1 hexanes/ethyl acetate, v/v) provided a homogeneous mixture of **15b/16b** (239.3 mg, 78%) that was analyzed by ^1H NMR spectroscopy. In a separate experiment, pure **15b** (74%) and **16b** (2%) were obtained (Table I, entry 8) by performing the chromatography with an eluting solvent of hexanes/ethyl acetate (5:1 v/v). The minor isomer **16b** was eluted first, followed by the major isomer **15b**. Recrystallization from benzene–hexanes provided analytically pure materials. These materials displayed the following physical properties.

***syn*-4-Acetoxy-3-[(tolylsulfonyl)amino]-2-iodoundecene (15b)**: white solid (mp 47–48 °C); IR ($CHCl_3$) 3282, 2927, 2856, 1746, 1599, 1434, 1335, 1232, 1162, 1093, 672 cm^{-1}; ^1H NMR δ 0.88 (br t, 3 H J = 6.4 Hz), 1.23 (br, 10 H), 1.45 (m, 2 H), 1.98 (s, 3 H), 2.42 (s, 3 H), 3.73 (br dd, 1 H, J = 5.8, 9.1 Hz), 5.02 (q, 1 H, J = 6.2 Hz), 5.11 (d, 1 H, J = 9.1 Hz), 5.73 (d, 1 H, J = 2.1 Hz), 6.18 (dd, 1 H, J = 0.9, 2.1 Hz), 7.28 (m, 2 H), 7.73 (m, 2 H); ^{13}C NMR δ 13.9, 20.7, 21.3, 22.4, 24.7, 28.86, 28.93, 31.0, 31.5, 64.8, 73.5, 109.2, 127.3, 128.9, 129.6, 138.1, 143.7, 171.1. Anal. Calcd for $C_{20}H_{30}NO_4SI$: C, 47.34; H, 5.96. Found: C, 47.89; H, 5.98.

***trans*-4-Acetoxy-3-[(tolylsulfonyl)amino]-2-iodoundecene (16b)**: white semisolid at room temperature; IR ($CHCl_3$) 3278, 2929, 2859, 1747, 1614, 1443, 1336, 1234, 1163, 1092, 911, 814, 668 cm^{-1}; ^1H NMR δ 0.88 (br t, 3 H, J = 6.4 Hz), 1.23 (br, 10 H), 1.45 (m, 2 H), 1.97 (s, 3 H), 2.42 (s, 3 H), 3.72 (br dd, 1 H, J = 6.8, 9.7 Hz), 4.87 (ddd, 1 H, J = 3.7, 6.8, 8.6 Hz), 5.18 (d, 1 H, J = 9.7 Hz), 5.72 (d, 1 H, J = 1.9 Hz), 6.13 (dd, 1 H, J = 0.8, 1.9 Hz), 7.28 (m, 2 H), 7.73 (m, 2 H); ^{13}C NMR δ 13.9, 20.7, 21.4, 22.4, 24.9, 28.9, 29.1, 29.6, 31.6, 63.6, 73.6, 109.0, 127.5, 129.6, 129.7, 137.5, 143.9, 170.4; exact mass calcd for $C_{20}H_{31}NO_4SI$ $(M + H)^+$ 508.1019, found 508.1013.

***syn*-1-Acetoxy-2-[(tolylsulfonyl)amino]-1-cyclohexyl-3-iodo-3-butene (15a)**: white solid (mp 149–150 °C); IR ($CHCl_3$) 2929, 1739, 1450, 1340 cm^{-1}; ^1H NMR δ 0.8–1.8 (m, 11 H), 1.98 (s, 3 H), 2.42 (s, 3 H), 4.02 (br dd, 1 H, J = 4.5, 9.2 Hz), 4.93 (dd, 1 H, J = 4.5, 6.2 Hz), 5.46 (d, 1 H, J = 9.2 Hz), 5.70 (d, 1 H, J = 2.2 Hz), 6.16 (dd, 1 H, J = 1.0, 2.2 Hz), 7.28 (m, 2 H), 7.74 (m, 2 H); ^{13}C NMR δ 20.4, 21.3, 25.4, 25.8, 26.9, 29.0, 37.6, 62.4, 76.7, 109.0, 127.3, 128.1, 129.6, 138.0, 143.7, 170.9. Anal. Calcd for $C_{19}H_{26}NO_4SI$: C, 46.44; H, 5.33. Found: C, 47.09; H, 5.39.

***trans*-1-Acetoxy-2-[(tolylsulfonyl)amino]-1-cyclohexyl-3-iodo-3-butene (16a)**: white solid (mp 199–200 °C); IR ($CHCl_3$) 2927, 1732, 1451, 1340 cm^{-1}; ^1H NMR δ 0.8–1.8 (m, 11 H), 2.00 (s, 3 H), 2.43 (s, 3 H), 3.67 (br dd, 1 H, J = 8.4, 10.0 Hz), 4.71

(dd, 1 H, J = 3.5, 8.4 Hz), 4.88 (d, 1 H, J = 10.0 Hz), 5.65 (d, 1 H, J = 1.9 Hz), 6.04 (dd, 1 H, J = 1.1, 1.9 Hz), 7.28 (m, 2 H), 7.73 (m, 2 H). Anal. Calcd for $C_{19}H_{26}NO_4SI$: C, 46.44; H, 5.33. Found: C, 46.75; H, 5.48.

***syn*-4-Acetoxy-3-[(tolylsulfonyl)amino]-2-iodo-6-methylheptene (15c)**: white solid (mp 92–93 °C); IR ($CHCl_3$) 2962, 1731, 1609, 1420, 1339, 1247, 1162, 1093, 814 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.88 and 0.92 (d each, 3 H each, J = 6.6 Hz each), 1.27 (m, 2 H), 1.45 (m, 1 H), 2.02 (s, 3 H), 2.45 (s, 3 H), 3.70 (ddd, 1 H, J = 0.9, 6.5, 9.1 Hz), 5.09 (d, 1 H, J = 9.1 Hz), 5.13 (m, 1 H), 5.74 (d, 1 H, J = 2.0 Hz), 6.20 (dd, 1 H, J = 0.9, 2.0 Hz), 7.26 (m, 2 H), 7.73 (m, 2 H); ^{13}C NMR δ 20.7, 21.3, 21.5, 22.9, 24.2, 40.0, 65.3, 72.0, 109.6, 127.4, 129.6, 138.1, 143.7, 171.4, 210.4. Anal. Calcd for $C_{17}H_{24}NO_4SI$: C, 43.88; H, 5.20. Found: C, 43.64; H, 5.44.

***trans*-4-Acetoxy-3-[(tolylsulfonyl)amino]-2-iodo-6-methylheptene (16c)**: white solid (mp 106–107 °C); IR ($CHCl_3$) 3035, 2962, 1733, 1609, 1429, 1342, 1262, 1160, 1090, 913 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.87 and 0.90 (d each, 3 H each, J = 6.6 Hz each), 1.27–1.60 (m, 3 H), 1.95 (s, 3 H), 2.42 (s, 3 H), 3.73 (ddd, 1 H, J = 1.0, 6.2, 9.1 Hz), 4.93 (d, 1 H, J = 9.1 Hz), 4.97 (dt, 1 H, J = 3.5, 6.2 Hz), 5.74 (d, 1 H, J = 2.0 Hz), 6.13 (dd, 1 H, J = 1.0, 2.0 Hz), 7.26 (m, 2 H), 7.72 (m, 2 H); ^{13}C NMR δ 20.7, 21.3, 23.2, 24.2, 38.3, 63.9, 71.9, 108.1, 127.5, 129.6, 137.4, 143.8, 170.5, 210.8. Anal. Calcd for $C_{17}H_{24}NO_4SI$: C, 43.88; H, 5.20. Found: C, 44.18; H, 5.31.

***syn*-4-Acetoxy-3-[(tolylsulfonyl)amino]-2-iodo-5-methylhexene (15d)**: white solid (mp 122–123 °C); IR ($CHCl_3$) 2970, 1733, 1612, 1420, 1338, 1251, 1160, 1093, 914 cm^{-1}; ^{1}H NMR δ 0.89 (d, 3 H, J = 6.8 Hz), 0.92 (d, 3 H, J = 6.8 Hz), 1.90 (m, 1 H), 2.00 (s, 3 H), 2.42 (s, 3 H), 3.91 (ddd, 1 H, J = 1.0, 5.8, 9.2 Hz), 4.89 (t, 1 H, J = 5.8 Hz), 5.24 (d, 1 H, J = 9.2 Hz), 5.68 (d, 1 H, J = 2.1 Hz), 6.15 (dd, 1 H, J = 1.0, 2.1 Hz), 7.28 (m, 2 H), 7.72 (m, 2 H); ^{13}C NMR δ 15.9, 19.1, 20.5, 21.4, 28.2, 63.2, 77.5, 109.5, 127.4, 128.6, 129.6, 138.2, 143.7, 171.3. Anal. Calcd for $C_{16}H_{22}NO_4SI$: C, 42.58; H, 4.91. Found: C, 43.08; H, 4.96.

***syn*-4-Acetoxy-3-[(tolylsulfonyl)amino]-5,5-dimethyl-2-iodohexene (15e)**: white solid (mp 153–154 °C); IR ($CHCl_3$) 2962, 1747, 1402, 1339, 1158, 1093, 947 cm^{-1}; ^{1}H NMR δ 1.03 (s, 9 H), 2.02 (s, 3 H), 2.43 (s, 3 H), 4.34 (br d, 1 H, J = 9.8 Hz), 4.94 (d, 1 H, J = 1.8 Hz), 5.52 (d, 1 H, J = 2.4 Hz), 5.62 (d, 1 H, J = 9.8 Hz), 5.94 (dd, 1 H, J = 1.1, 2.4 Hz), 7.27 (m, 2 H), 7.74 (m, 2 H); ^{13}C NMR δ 20.6, 21.4, 26.3, 35.1, 61.4, 78.4, 110.2, 127.0, 127.5, 129.6, 137.9, 143.8, 170.3. Anal. Calcd for $C_{17}H_{24}NO_4SI$: C, 43.88; H, 5.20. Found: C, 43.72; H, 5.46.

***syn*-1-Acetoxy-2-[(tolylsulfonyl)amino]-3-iodo-1-phenyl-3-butene (15f)**: colorless semisolid; IR ($CHCl_3$) 3031, 1742, 1702, 1423, 1364, 1218, 1098, 1032, 925 cm^{-1}; ^{1}H NMR δ 2.03 (s, 3 H), 2.39 (s, 3 H), 3.97 (ddd, 1 H, J = 0.9, 7.4, 8.8 Hz), 5.46 (d, 1 H, J = 8.8 Hz), 5.57 (d, 1 H, J = 2.1 Hz), 5.92 (d, 1 H, J = 7.4 Hz), 5.98 (dd, 1 H, J = 0.9, 2.1 Hz), 7.18–7.32 (m, 7 H), 7.63 (m, 2 H); ^{13}C NMR δ 20.7, 21.3, 66.6, 75.1, 108.9, 127.20, 127.24, 128.6, 128.8, 129.5, 130.0, 136.1, 137.7, 143.5, 170.5; exact mass calcd for $C_{19}H_{20}NO_4SI$ (M + H)$^+$ 486.0236, found 486.0276.

General Procedure for the Preparation of Oxazolidinones 12. The procedure described below for the preparation of **12b** is general. To a solution of the alcohol **8b** (237.0 mg, 1.41 mmol) in ether (4 mL) at 0 °C was added trichloroacetyl isocyanate (0.19 mL, 1.5 mmol). After stirring for 10 min at 0 °C, solid I_2 (358 mg, 2.82 mmol) and solid K_2CO_3 (780 mg, 5.64 mmol) were added, and the resulting mixture was stirred at room temperature until TLC analysis indicated the absence of the diiodide (48 h). Water (4 mL) was added and the excess I_2 was decomposed by the addition of 10% aqueous $NaHSO_3$. The aqueous layer was made neutral by the addition of saturated aqueous $NaHCO_3$. The resulting mixture was extracted with ether (3 × 10 mL) and the combined organics were dried and concentrated. The crude reaction mixture was analyzed by ^{1}H NMR spectroscopy (Table I, entry 16) and then subjected to column chromatography (hexanes/ethyl acetate, 3:1 to 3:2, v/v). The major trans isomer **12b** was eluted first, followed by the minor cis isomer **14b**. Recrystallization from hexanes–ethyl acetate–ether provided analytically pure samples of the oxazolidinones in the yields indicated in Table I. These materials displayed the following physical properties.

***trans*-4-(1-Iodoethylene)-5-*n*-heptyl-2-oxazolidinone (12b)**: colorless crystals (mp 60–61 °C); IR (KBr) 3350, 2954, 2940, 2920, 2850, 1736, 1704, 1700, 1614 cm^{-1}; ^{1}H NMR δ 0.84 (t, 3 H, J = 7 Hz), 1.24–1.47 (m, 8 H), 1.72 (m, 2 H), 3.77 (br d, 1 H, J = 4.5 Hz), 4.47 (q, 1 H, J = 4.5 Hz), 5.90 (d, 1 H, J = 2.2 Hz), 6.43 (dd, 1 H, J = 1.3, 2.2 Hz), 7.01 (br s, 1 H); ^{13}C NMR δ 14.2, 22.8, 24.8, 29.26, 29.34, 31.9, 35.0, 66.5, 82.7, 112.4, 127.9, 159.8. Anal. Calcd for $C_{12}H_{20}NO_2I$: C, 42.72; H, 5.98. Found: C, 42.67; H, 5.85.

***cis*-4-(1-Iodoethylene)-5-*n*-heptyl-2-oxazolidinone (14b)**: colorless crystals (mp 91–93 °C); IR (KBr) 3240, 3120, 2950, 2920, 2854, 1730, 1686, 1396, 1230 cm^{-1}; ^{1}H NMR δ 0.83–0.86 (m, 3 H), 1.19–1.83 (m, 12 H), 4.35 (d, 1 H, J = 7.8 Hz), 4.70 (dt, 1 H, J = 4.1, 7.8 Hz), 6.06 (d, 1 H, J = 2.1 Hz), 6.43 (m, 2 H); ^{13}C NMR δ 14.3, 23.2, 26.9, 29.4, 29.9, 32.4, *64.0, 64.1*, 80.1, 109.9, 130.1, 159.0; exact mass calcd for $C_{12}H_{21}NO_2I$ (M + H)$^+$ 338.0617, found 338.0614.

***trans*-4-(1-Iodoethylene)-5-cyclohexyl-2-oxazolidinone (12a)**: colorless crystals (mp 103–104 °C); IR (KBr) 3600–3300, 3250, 2930, 2850, 1748, 1715, 1711 cm^{-1}; ^{1}H NMR δ 1.09–1.24 (m, 5 H), 1.64–1.82 (m, 6 H), 3.87 (d, 1 H, J = 4.1 Hz), 4.03 (br t, 1 H, J = 4.1 Hz), 5.87 (br s, 1 H), 6.41 (br s, 1 H), 6.98 (br s, 1 H); ^{13}C NMR δ 25.6, 25.8, 26.2, 27.3, 28.1, 42.0, 86.1, 113.7, 127.8, 159.7. Anal. Calcd for $C_{11}H_{16}NO_2I$: C, 41.12; H, 5.02. Found: C, 41.16; H, 5.04.

***trans*-4-(1-Iodoethylene)-5-isopropyl-2-oxazolidinone (12d)**: colorless crystals (mp 90–91 °C); IR (KBr) 3250, 3170, 3090, 2980, 2960, 1757, 1720, 1614 cm^{-1}; ^{1}H NMR δ 1.03 (d, 6 H, J = 6.9 Hz), 2.00 (m, 1 H), 3.89 (d, 1 H, J = 4.4 Hz), 4.09 (br t, 1 H, J = 4.4 Hz), 5.93 (d, 1 H, J = 2.1 Hz), 6.48 (br d, 1 H, J = 2.2 Hz), 7.13 (br s, 1 H); ^{13}C NMR (100 MHz, d_6-acetone) δ 17.2, 17.9, 33.0, *63.9, 64.0*, 86.22, *116.75, 116.79*, 128.5, *158.1, 158.2*. Anal. Calcd for $C_8H_{12}NO_2I$: C, 34.16; H, 4.30. Found: C, 34.20; H, 4.27.

***trans*-4-(1-Iodoethylene)-5-*tert*-butyl-2-oxazolidinone (12e)**: colorless crystals (mp 129–130 °C); IR (KBr) 3460–3330, 3255, 2963, 1752, 1717, 1230 cm^{-1}; ^{1}H NMR δ 1.00 (s, 9 H), 3.82 (d, 1 H, J = 4.2 Hz), 3.93 (d, 1 H, J = 4.2 Hz), 5.93 (d, 1 H, J = 2.2 Hz), 6.46 (dd, 1 H, J = 2.2, 0.5 Hz), 6.95 (s, 1 H); ^{13}C NMR (100 MHz) δ 24.5, 34.4, 61.8, 89.0, 114.8, 128.1, 159.3; exact mass calcd for $C_9H_{15}NO_2I$ (M + H)$^+$ 296.0148, found 296.0145.

***trans*-4-(1-Iodoethylene)-5-phenyl-2-oxazolidinone (12f)**: colorless crystals (mp 139–140 °C); IR (KBr) 3325–3200, 3146, 1747, 1726 cm^{-1}; ^{1}H NMR δ 4.01 (br d, 1 H, J = 5.1 Hz), 5.27 (br d, 1 H, J = 5.1 Hz), 6.01 (t, 1 H, J = 2.1 Hz), 6.45 (dd, 1 H, J = 2.1, 1.1 Hz), 7.20 (br s, 1 H), 7.40 (br, 5 H); ^{13}C NMR (d_6-acetone) δ *69.3, 69.4*, 83.0, 114.4, 127.0, 129.5, 130.0, 139.8, 158.0. Anal. Calcd for $C_{11}H_{10}NO_2I$: C, 41.91; H, 3.20. Found: C, 41.94; H, 3.32.

Preparation of Diiodides 21a,b and 22a,b. 21a/22a. When the iodocyclization reaction (see above) of **9b** (157.3 mg, 0.430 mmol) was stopped after 30 min, workup and chromatography (hexanes/ethyl acetate, 2:1, v/v) provided a mixture of the diiodides **21a/22a** (187.9 mg, 71%) as a pale yellow oil that decomposed rapidly at room temperature or when stored. This mixture exhibited the following properties: ^{1}H NMR (400 MHz) δ 0.85 (t, 6 H, J = 6.9 Hz), 1.15–1.65 (m, 24 H), 2.43 (s, 3 H), 2.44 (s, 3 H), 3.96 (d, 1 H, J = 10.9 Hz), 4.23 (dd, 1 H, J = 0.8, 10.8 Hz), 4.37 (dd, 1 H, J = 1.0, 10.8 Hz), 4.72 (d, 1 H, J = 10.9 Hz), 5.13 (dt, 1 H, J = 7.8, 6.0 Hz), 5.20 (dt, 1 H, J = 9.5, 6.8 Hz), 5.86 (br d, 1 H, J = 7.8 Hz), 5.92 (d, 1 H, J = 9.5 Hz), 7.30–7.36 (m, 4 H), 7.6 (br, 2 H), 7.85–7.91 (m, 4 H); FAB MS (NBA matrix) obsd (M + Na)$^+$ at m/e 642.

21b/22b. In a manner identical with the preparation of **12b**, **8b** (108.0 mg, 0.60 mmol) in ether (1.5 mL) was treated with $OCNCOCCl_3$. When TLC analysis indicated the absence of starting material (10 min), methanol (4 mL) and saturated aqueous K_2CO_3 (4 mL) were added, and the resulting mixture was stirred at room temperature for 2 h. The volatile organics were removed in vacuo and the residual aqueous solution was extracted with ether (3 × 15 mL). The combined organics were dried, concentrated, and subjected to column chromatography (hexanes/ethyl acetate, 5:1, v/v). The carbamate **20** was obtained (110.2 mg, 81%) as a white solid (mp 26–27 °C; ^{1}H NMR δ 0.85 (t, 3 H, J = 6.4 Hz), 1.2–1.6 (m, 12 H), 4.81–4.84 (m, 4 H), 5.08–5.21 (m, 2 H); ^{13}C NMR δ 13.8, 22.4, 25.0, 29.0, 29.1, 31.6, 34.2, 72.5, 77.1, 91.1, 156.8, 188.1; FAB MS (NBA matrix) 212 (M + H)$^+$) and was used immediately in the next step. A solution of the carbamate **20** (64.3 mg, 0.30 mmol) in ether (0.5 mL) and saturated aqueous $NaHCO_3$ (0.25 mL) was treated with solid I_2 (154 mg, 0.61 mmol), and the

resulting mixture was stirred at room temperature for 1.5 h. Aqueous 10% $NaSO_3$ was added until the solution became colorless, and the resulting mixture was extracted with ether (3 × 20 mL). The combined organics were dried and concentrated. The residual material was subjected to column chromatography (hexanes/ethyl acetate, 3:1, v/v) to provide the *Z* diiodide **21b** (49.4 mg, 36%) and the *E* diiodide **22b** (32.3 mg, 23%). These materials exhibited the following physical properties.

***Z* diiodide 21b**: white solid (mp 59–60 °C); IR (KBr) 3420, 2953, 2856, 1685, 1613, 1048 cm^{-1}; ^1H NMR δ 0.84 (t, 3 H, *J* = 6.8 Hz), 1.1–1.4 (m, 10 H), 1.5–1.6 (m, 2 H), 4.28 (d, 1 H, *J* = 10.7 Hz), 4.40 (d, 1 H, *J* = 10.7 Hz), 5.00 (br s, 2 H), 5.09 (m, 1 H), 5.96 (d, 1 H, *J* = 7.7 Hz); ^{13}C NMR δ 13.9, 17.0, 22.4, 24.4, 28.9, 29.2, 31.6, 33.2, 79.2, 104.1, 138.2, 156.7; exact mass calcd for $C_{12}H_{20}NO_4I_2$ $(M - H)^+$ 463.9584, found 463.9556.

***E* diiodide 22b**: colorless oil; IR (KBr) 3430–3200, 2950, 2860, 1685, 1613, 1400, 1320, 1048 cm^{-1}; ^1H NMR δ 0.89 (t, 3 H, *J* = 6.6 Hz), 1.2–1.4 (m, 10 H), 1.5–1.7 (m, 2 H), 4.09 (d, 1 H, *J* = 10.6 Hz), 4.61 (br s, 2 H), 4.90 (d, 1 H, *J* = 10.6 Hz), 5.26 (dt, 1 H, *J* = 9.5, 6.7 Hz), 6.10 (d, 1 H, *J* = 9.5 Hz); ^{13}C NMR δ 11.2, 14.1, 22.6, 24.7, 29.1, 31.4, 31.8, 33.4, 71.7, 103.1, 142.5, 156.5; exact mass calcd for $C_{12}H_{20}NO_4I_2$ $(M - H)^+$ 463.9584, found 463.9621.

General Procedure for the Ozonolysis of 12. The procedures described below for the ozonolysis of vinyl iodide **12b** are representative.

Acids 25. In a three-necked flask equipped with a drying tube, a solution of the vinyl iodide **12b** (136.0 mg, 0.4 mmol) dissolved in CH_2Cl_2 (8 mL) was cooled to −78 °C. Ozone was bubbled through this well-stirred solution until the solution turned blue (35 min). The solution was warmed to room temperature and 10% aqueous KOH (2 mL) was added. The mixture was extracted with ether (3 × 15 mL) to remove the nonacidic organic components and then the aqueous layer was acidified (~pH 3) with 10% aqueous H_2SO_4. This solution was extracted with ethyl acetate (3 × 15 mL) and the combined organics were dried and concentrated. Hexane (~5 mL) was added and the insoluble carboxylic acid **25b** was removed by filtration (92.0 mg, 99%). The materials prepared in this manner gave satisfactory peak matches (HRMS) and displayed ^1H and ^{13}C NMR spectra that indicated the absence of any organic byproducts.

***trans*-5-*n*-Heptyl-1-oxo-2-oxazolidine-4-carboxylic acid (25b)**: white solid (mp 123–135 °C dec); IR (KBr) 3600–2900, 2940, 2860, 1735, 1650, 1185 cm^{-1}; ^1H NMR (d_6-acetone) δ 0.84–0.88 (br t, 3 H), 1.29–1.49 (m, 10 H), 1.78 (br q, 2 H, *J* = 6.3 Hz), 4.14 (d, 1 H, *J* = 4.8 Hz), 4.54 (dd, 1 H, *J* = 4.8, 6.3 Hz), 6.97 (br s, 1 H); ^{13}C NMR (CD_3OD) δ 14.3, 22.8, 23.6, 25.4, 30.2, 32.8, 36.3, 60.3, 81.3, 161.5, 174.5; exact mass calcd for $C_{11}H_{20}NO_4$ $(M + H)^+$ 230.1392, found 230.1392.

***trans*-5-Cyclohexyl-1-oxo-2-oxazolidine-4-carboxylic acid (25a)**: white solid (mp 147–148 °C); IR (KBr) 3600–3200, 2928, 2854, 1762–1736 cm^{-1}; ^1H NMR (400 MHz, d_6-acetone) δ 1.09–1.34 (m, 5 H), 1.63–1.87 (m, 6 H), 4.23 (d, 1 H, *J* = 4.0 Hz), 4.34 (dd, 1 H, *J* = 4.4, 5.9 Hz), 7.02 (br s, 1 H); ^{13}C NMR (100 MHz, d_6-acetone) δ 26.2, 26.3, 26.9, 27.7, 28.4, 43.1, 56.7, 83.2, *158.67*, *158.72*, 172.8; exact mass calcd for $C_{10}H_{16}NO_4$ $(M + H)^+$ 214.1080, found 214.1080. Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09. Found: C, 55.63; H, 7.08.

***trans*-5-Isopropyl-1-oxo-2-oxazolidine-4-carboxylic acid (25d)**: colorless oil; IR (KBr) 3600–3200, 2968, 1759–1727, 1230 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 1.03 (d, 6 H, *J* = 6.9 Hz), 1.99 (m, 1 H), 4.15 (d, 1 H, *J* = 4.5 Hz), 4.39 (dd, 1 H, *J* = 4.5, 5.9 Hz); ^{13}C NMR (CD_3OD) δ 16.8, 17.4, 33.9, 57.7, 85.6, 159.6, 174.4; exact mass calcd for $C_7H_{12}NO_4$ $(M + H)^+$ 174.0766, found 174.0769. Anal. Calcd for $C_7H_{11}NO_4$: C, 48.55; H, 6.40. Found: C, 49.89; H, 6.55.

***trans*-5-*tert*-Butyl-1-oxo-2-oxazolidine-4-carboxylic acid (25e)**: white solid (mp 174–175 °C); IR (KBr) 3300, 2965, 1752–1736 cm^{-1}; ^1H NMR (d_6-acetone) δ 0.97 (s, 9 H), 4.26 (s, 2 H), 7.70 (br s, 1 H); ^{13}C NMR (d_6-acetone) δ 24.1, 35.4, 55.1, 86.8, 163.3, 173.4; exact mass calcd for $C_8H_{14}NO_4$ $(M + H)^+$ 188.0923, found 188.0924.

***trans*-5-Phenyl-1-oxo-2-oxazolidine-4-carboxylic acid (25f)**: white solid (mp 200–210 °C dec); IR (KBr) 3300, 1756–1731 cm^{-1}; ^1H NMR (CD_3OD) δ 4.30 (d, 1 H, *J* = 4.9 Hz), 5.64 (d, 1 H, *J* = 4.9 Hz), 7.43 (br s, 5 H); ^{13}C NMR (CD_3OD) δ 62.8, 81.4, 126.8, 130.3, 140.6, 161.2, 173.5; exact mass calcd for $C_{10}H_9NO_4$ (M^+) 207.0532, found 207.0540. Anal. Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.38. Found: C, 57.39; H, 4.84.

Methyl Esters 26. A solution of the vinyl iodide **12b** (44.0 mg, 0.14 mmol) in methanol (3 mL) at −78 °C was ozonized to completion as above (blue end point). Excess ozone was displaced by a stream of oxygen, the cold bath was removed, and the solution was stirred for 1 h. Methanol was removed in vacuo and the brown residue was dissolved in ethyl acetate (5 mL). Water (3 mL) was added, followed by 10% aqueous KOH until the solution was basic. The organic layer was removed and the aqueous phase was extracted with ethyl acetate (3 × 5 mL). The aqueous phase was re-acidified with 10% aqueous H_2SO_4 and extracted with ethyl acetate (3 × 10 mL). The combined organics were dried and concentrated. The residual material was subjected to column chromatography (methanol/CH_2Cl_2, 25:1, v/v) and provided the methyl ester **26b** (22.0 mg, 65%) as a colorless oil.

Methyl *trans*-5-*n*-heptyl-1-oxo-2-oxazolidine-4-carboxylate (26b): colorless oil; IR 3270, 2955, 2924, 2853, 1763, 1753, 1744, 1222 cm^{-1}; ^1H NMR δ 0.89 (br t, 3 H), 1.25–1.41 (m, 10 H), 1.79 (m, 2 H), 3.82 (s, 3 H), 4.02 (d, 1 H, *J* = 5.0 Hz), 4.63 (dt, 1 H, *J* = 5.0, 5.7 Hz), 5.53 (br s, 1 H); ^{13}C NMR δ 13.87, 22.4, 24.2, 28.9, 29.6, 31.5, 35.2, 53.0, 58.6, 79.2, 158.3, 170.8; exact mass calcd for $C_{12}H_{22}NO_4$ $(M + H)^+$ 244.1549, found 244.1558.

Methyl *trans*-1-oxo-5-phenyl-2-oxazolidine-4-carboxylate (26f): colorless oil; IR 3425–3230, 2940, 1840, 1762–1735 cm^{-1}; ^1H NMR (CD_3OD) δ 3.84 (s, 3 H), 4.36 (d, 1 H, *J* = 4.8 Hz), 5.66 (d, 1 H, *J* = 4.8 Hz), 7.43 (m, 6 H); ^{13}C NMR (CD_3OD) δ 62.8, 76.3, 81.1, 126.9, 130.3, 130.4, 161.7, 172.2; exact mass calcd for $C_{11}H_{12}NO_4$ $(M + H)^+$ 222.0766, found 222.0759.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada and the University of Toronto is gratefully acknowledged. We would like to thank Dr. Alan Lough of this department for carrying out the X-ray crystallographic analyses.

Supplementary Material Available: ORTEP representations and crystallographic data (bond distances, bond angles, torsion angles) for **12b** and **15a** and ^1H NMR spectra for **8a–f**, **9a–f**, **12e**, **15f**, **16b**, **21a/22a**, **21b**, **22b**, **25b**, **25e**, **26b**, and **26f** (30 pages). Ordering information is given on any current masthead page.