Stereochemistry of the Epoxidations of Acyclic Allylic Amides. Applications toward the Synthesis of 2,3,6-Trideoxy-3-aminohexoses[1]

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The stereochemistry of the epoxidation of several acyclic allylic amides is described. Diastereoselectivity in the (*Z*)-allylic amide series (compound **1**) proved to be dependent both on the amide functionality and epoxidation reagent. The threo epoxide **3** was highly favored (95:5) with MCPBA as oxidant when phenylurea **1d** was used as substrate. High threo selectivity (88:12) also was realized in the $Mo(CO)_6$-catalyzed epoxidation of trichloroacetamide **1a**. Results in the (*E*)-allylic amide series (compound **2**), however, are much less sensitive to the reagent and amide functionality. Epoxidation of **2a** either with peracids or $Mo(CO)_6$–TBHP provided threo epoxide **5a** with 76–78% stereoselectivity. This method was applied to the synthesis of *N*-benzoylristosamine (epoxidation of **21**) and precursors to *N*-benzoyldaunosamine and *N*-benzoyl-3-amino-2,3,6-trideoxy-*xylo*-hexose. Results obtained with the daunosamine precursor **30** show that diminished stereoselectivity will occur if the substrate contains functionality that can hydrogen bond to the amide NH.

The epoxidation of acyclic allylic alcohols is an important transformation in organic synthesis.[4,5] By virtue of the excellent diastereoselectivity realized in many cases, this reaction and subsequent manipulations of the 2,3-epoxy alcohol unit have found widespread application in the synthesis of stereochemically adorned acyclic systems.[6,7] As an extension of our work on the synthesis of rare monosaccharides,[1,8] we became interested in the epoxidation of acyclic allylic amides as a strategy for synthesis of amino sugars.[9] Although it had long been recognized that the amide functionality is an excellent directing group in the Henbest sense,[4d,10] prior to the initiation of our studies no information was available regarding the stereochemistry of epoxidation of acyclic allylic amides.[11]

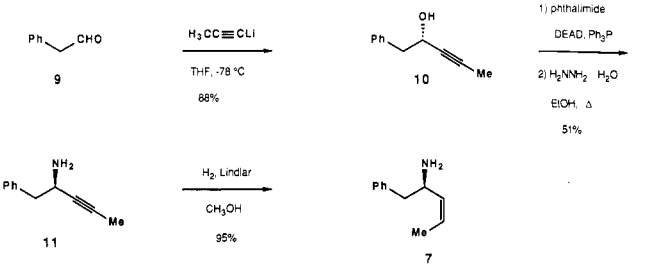
We report herein the results of epoxidation of two series of model allylic amides and applications of this method to the synthesis of *N*-benzoylristosamine and precursors to *N*-benzoyldaunosamine and *N*-benzoyl-3-amino-2,3,6-trideoxy-*xylo*-hexose (*N*-benzoyl-4-*epi*-ristosamine).[12]

Stereochemical Studies. Secondary allylic amines **7** and **8**, prepared as summarized in Schemes I and II, served as the model systems for the initial phase of these studies. Amide, urethane, and phenylurea derivatives **1a–d** and **2c,d** were synthesized by using standard procedures (see Experimental Section) and then were epoxidized by using either peracids [MCPBA or 3,5-dinitroperoxybenzoic acid (3,5-DNPBA)[13]] or $Mo(CO)_6$/TBHP.[14,15] The results of these experiments are recorded in Table I.

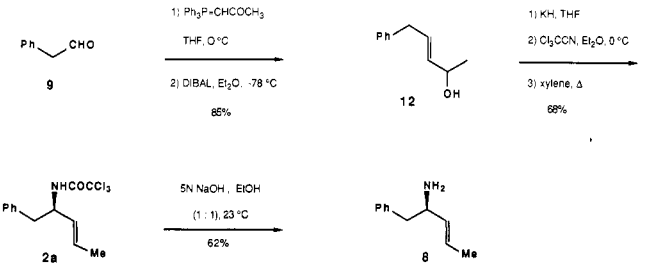
The diastereoselectivity of the epoxidation of (*Z*)-allylic amides **1** proved to be dependent both on the amide functionality and epoxidation reagent. Best results (95:5) with MCPBA as oxidant were obtained when phenylurea **1d** was used as substrate (entry 6). Amides **1a,b** and urethane **1c** showed substantially reduced selectivity under comparable conditions. On the other hand, $Mo(CO)_6$-catalyzed epoxidation of trichloroacetamide **1a** also proceeded with excellent threo selectivity (88:12; 90% yield (entry 2)). Since a $Cl_3CCONHR$ group is more easily manipulated than a phenylurea, the conditions specified in entry 2 were viewed as optimal for the epoxidation of (*Z*)-allylic amine derivatives. The selectivity, at least in this case, is similar to that obtained from (*Z*)-allylic alcohols under comparable conditions.[5d,e]

The diastereoselectivity in the (*E*)-allylic amide series (**2**, entries 7–13) proved to be much less sensitive to reagent, amide functionality, and experimental conditions.

Scheme I. Synthesis of (*Z*)-Allylic Amine 7



Scheme II. Synthesis of (*E*)-Allylic Amine 8



Essentially identical results were obtained in the epoxidation of trichloroacetamide **2a** using either peracids

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(1) Total Synthesis of Carbohydrates. 5. For part 4, see: Roush, W. R.; Hagadorn, S. M. *Carbohydr. Res.* **1985**, *136*, 187.

(2) Holder of the Firmenich Career Development Chair in Natural Products Chemistry, 1981–84; Fellow of the Alfred P. Sloan Foundation, 1982–86.

(3) Portions of this work are described in the Ph.D. Thesis of R. J. Brown, Massachusetts Institute of Technology, Cambridge, MA 1983.

(4) Reviews: (a) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. (b) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589. (c) Behrens, C. H.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67. (d) Berti, G. *Top. Stereochem.* **1973**, *7*, 93. (e) Buchanan, J. G.; Sable, H. Z. *Sel. Org. Transform.* **1972**, *2*, 1.

(5) (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (b) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *Ibid.* **1981**, *103*, 464. (c) Martin, V. S.; Woodward, S. S.; Katsuki, T.; Yamada, T.; Ikeda, M.; Sharpless, K. B. *Ibid.* **1981**, *103*, 6237. (c) Mihelich, E. D.; Daniels, K.; Eichhoff, D. J. *Ibid.* **1981**, *103*, 7690. (d) Mihelich, E. D. *Tetrahedron Lett.* **1979**, 4729. (e) Rossiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. *Ibid.* **1979**, 4733. (f) Tomioka, H.; Suzuki, T.; Oshima, K.; Nozaki, H. *Ibid.* **1982**, *23*, 3387. (g) Narula, A. S. *Ibid.* **1982**, *23*, 5579.

(6) (a) McGarvey, G. J.; Kimura, M.; Oh, T.; Williams, J. M. *J. Carbohydr. Chem.* **1984**, *3*, 125. (b) Zamojski, A.; Banaszek, A.; Grynkiewicz, G. *Adv. Carbohydr. Chem. Biochem.* **1982**, *40*, 1. (c) Barlett, P. A. *Tetrahedron* **1980**, *36*, 3.

(7) For leading references on the regioselective manipulation of 2,3-epoxy alcohols, see: (a) Roush, W. R.; Adam, M. A. *J. Org. Chem.* **1985**, *50*, 3752. (b) Behrens, C. H.; Ko, S. Y.; Sharpless, K. B.; Walker, F. J. *Ibid.* **1985**, *50*, 5687. (c) Behrens, C. H.; Sharpless, K. B. *Ibid.* **1985**, *50*, 5696.

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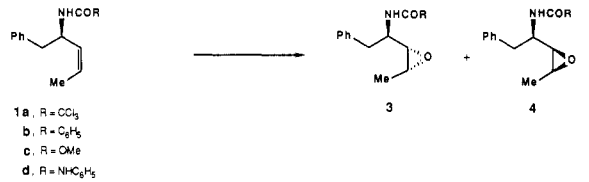
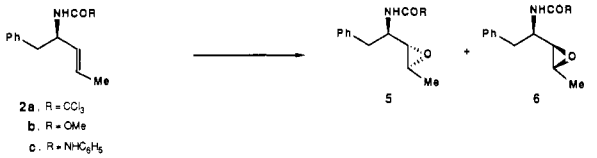
Table I



entry	substr	conditions	yield[a], %	ratio[b] 3:4
1	1a	MCPBA, CH_2Cl_2, 0 → 25 °C	83–85	75:25
2	1a	$Mo(CO_6$ (0.1 equiv), TBHP (7 equiv), C_6H_6, reflux	91	88:12[c]
3	1b	MCPBA, CH_2Cl_2, 0 °C	72	77:23[d]
4	1b	$Mo(CO)_6$ (0.1 equiv), TBHP (8 equiv), C_6H_6, reflux	23	86:14[d]
5	1c	MCPBA, CH_2Cl_2, 0 °C	90	67:33
6	1d	MCPBA, CH_2Cl_2, 0 °C	75	>95:5



entry	substr	conditions	yield,[a] %	ratio[b] 5:6
7	2a	$Mo(CO)_6$ (0.1 equiv), TBHP (3 equiv), C_6H_6, reflux	89	75:25
8	2a	MCPBA, CH_2Cl_2, 0 °C	77[e]	76:24
9	2a	MCPBA, C_6H_6, 0 °C		78:22
10	2a	3,5-DNPBA, CH_2Cl_2, −20 °C		76:24
11	2a	3,5-DNPBA, CH_2Cl_2, 0 C		78:22
12	2b	MCPBA, CH_2Cl_2, 23 °C	79	78:22
13	2c	MCPBA, CH_2Cl_2, 0 °C	88	60:40[f]

[a] Combined yield of products isolated by chromatography. [b] Product ratios were determined by 250-MHz ^1H NMR analysis of the crude reaction products. [c] The minor reaction product in this case is a mixture of **4a** and oxazolidine **14a** formed from **4a** under the reaction conditions. [d] The minor product in this case was oxazolidine **14b**. [e] The products from entires 8–11 were combined prior to chromatography. [f] The ratio of **5c** and several products presumably deriving from epoxide opening of **6c**.

or $Mo(CO)_6$–TBHP (entries 7–11). Nevertheless, it is noteworthy that the selectivity of these reactions (ca. 75:25 mixtures of **5** and **6**) is somewhat greater than that generally observed with (*E*)-allylic alcohols under comparable conditions.[5d,e]

The stereochemistry of epoxide **3d** was established by an X-ray crystal structure determination.[16] The ORTEP drawing reproduced in Figure 1 clearly shows that the C_3–C_4 relationship is threo.

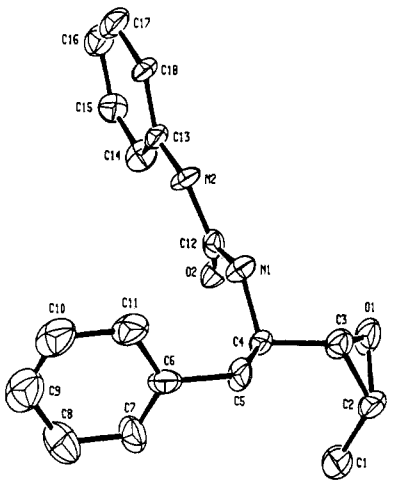


Figure 1. ORTEP representation of epoxide **3d**.

Stereochemical assignments for **3a,b** **4a,b** and **5a** were made following conversion to the corresponding oxazolidine derivatives **13–15**. *cis*-Oxazolidines **13** and **15** show $J_{2,3}$ = 9.5 Hz, whereas for *trans*-oxazolidine **14**, $J_{2,3}$ is 5–6 Hz. These data are consistent with the dihedral angles measured by using Drieding molecular models (0° for **13**/**15** and roughly 120° for **14**) and are in agreement with NMR data for related compounds.[17] Since the epoxides must open with inversion of configuration at C(3), the stereochemistry of **3a,b**, **4a,b**, and **5a** must be as indicated. We

(8) (a) Roush, W. R.; Brown, R. J.; DiMare, M. *J. Org. Chem.* **1983**, *48*, 5083. (b) Roush, W. R.; Brown, R. J. *Ibid.* **1983**, *48*, 5093.

(9) For a recent review of the synthesis of amino sugars, see: (a) Hauser, F. M.; Ellenberger, S. R. *Chem. Rev.* **1986**, *86*, 35. (b) See also ref 6a.

(10) (a) Goodman, L.; Winstein, S.; Bochan, R. *J. Am. Chem. Soc.* **1958**, *80*, 4312. (b) Hasegawa, A.; Sable, H. Z. *J. Org. Chem.* **1966**, *31*, 4154.

(11) (a) Ohfune, Y.; Kurokawa, N. *Tetrahedron Lett.* **1984**, *25*, 1587. These authors described the epoxidations of several 2-(acylamino)-3-butenol derivatives. The stereoselectivity observed in these reactions, however, appears to be a consequence of the directing influence of the homoallylic alcohol functionality. For more recent examples, see: (b) Shaw, K. J.; Luly, J. R.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 4515. (c) Hauser, F. M.; Ellenberger, S. R.; Glusker, J. P.; Smart, C. J.; Carrell, H. L. *J. Org. Chem.* **1986**, *51*, 50. (d) Luly, J. R.; Dellaria, J. F.; Plattner, J. J.; Soderquist, J. L.; Yi, N. *Ibid.* **1987**, *52*, 1487.

(12) All chiral compounds reported in this paper are racemic.

(13) Rastetter, W. H.; Richard, T. J.; Lewis, M. D. *J. Org. Chem.* **1978**, *43*, 3163.

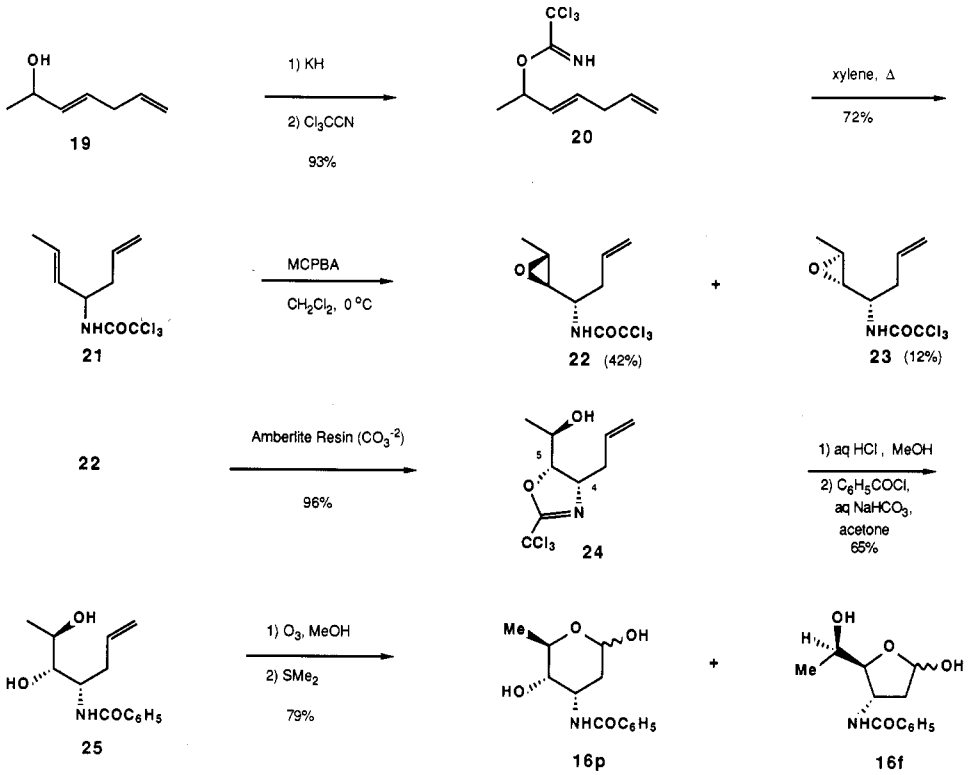
(14) (a) Tanaka, S.; Yamamoto, H.; Nozaki, H.; Sharpless, K. B.; Michaelson, R. C.; Cutting, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 5254. (b) Sharpless, K. B.; Michaelson, R. C. *Ibid.* **1973**, *95*, 6136.

(15) Attempted epoxidation of **2a** with $VO(acac)_2$ and TBHP (CH_2Cl_2, 23 °C, 2 days) gave no reaction, whereas use of $Ti(O\text{-}i\text{-}Pr)_4$ and TBHP led to a complex mixture of products.

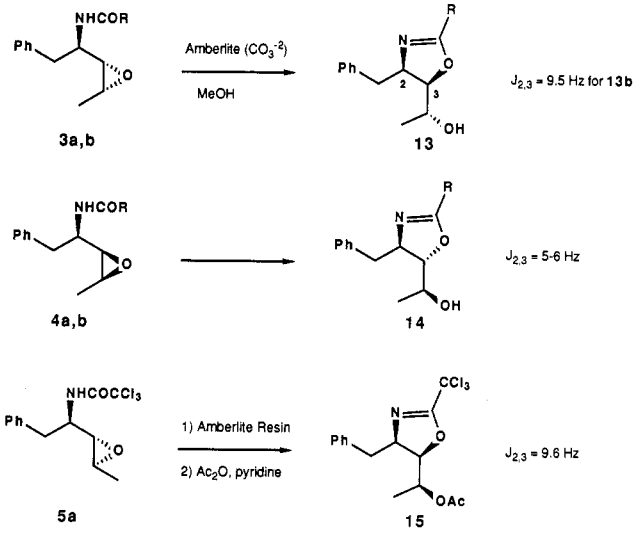
(16) We thank Dr. John C. Dewan of the MIT X-ray facility for the crystal structure determination and the Division of Research Resources (NIH Grant S10 RR 02243) for the funds used to purchase the X-ray diffractometer.

(17) (a) Cardillo, G.; Orena, M.; Sandri, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1489. (b) Meyers, A. I.; Smith, R. K.; Whitten, C. E. *J. Org. Chem.* **1979**, *44*, 2250.

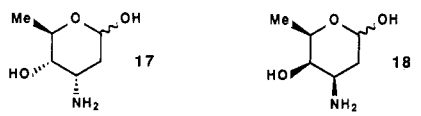
Scheme III. Synthesis of *N*-Benzoylristosamine (16p,f)



concluded that the stereochemistry of the major epoxide from each experiment summarized in Table I is threo.[18]



Synthesis of *N*-Benzoylristosamine (16). In order to gain additional insight into the stereochemistry of the amide directed epoxidation reaction, we undertook the synthesis of *N*-benzoylristosamine (**16**) summarized in Scheme III. Ristosamine (**17**), a rare amino sugar first



isolated during degradation studies of the antibiotic ristomycin,[19] is of considerable interest as an analogue of daunosamine (**18**) which is an important sugar component of several anthracycline antitumor antibiotics.[20,21] The readily available allylic alcohol **19**[8b] was selected as the starting material for this synthesis.[22] Since we had already resolved **19** by using the Sharpless kinetic resolution procedure,[5c] this synthesis would be potentially enantioselective.

Allylic amide **21** was prepared from **19** in 67% yield by using Overman's procedure.[23] The epoxidation of **21** was best accomplished by using MCPBA in CH_2Cl_2 at 0 °C, which provided threo epoxy amide **22** in 42% yield along with 12% of the erythro diastereomer **23**. Approximately 10% of a mixture of diepoxides was also produced, indicating that the site selectivity of this reaction was roughly 5:1. Although we had hoped that improved results would be realized by using $Mo(CO)_6$ and TBHP (1 equiv), this procedure gave threo epoxide **22** in low yield (23–32% based on unrecovered **21**). When greater amounts of TBHP were employed, the unwanted diepoxide was produced and the yield of **22** was not improved.

Smooth α-opening of the epoxide occurred when **22** was treated with a basic Amberlite resin (IR-400, CO_3^{2-} form) in MeOH.[17a] The 4,5-cis stereochemistry of **24**, and hence the threo relationship in **22**, was assigned on the basis of

(18) The stereochemistry of **3c**, **4c**, **5b**, and **6b** has not been determined rigorously. The assignments in these cases are by analogy to those that are summarized in text.

(19) (a) Lomakina, N. N.; Szpiridonova, I. A.; Bognar, R.; Puskas, M.; Sztaricskai, F. *Antibiotiki* **1968**, *13*, 975. (b) Bognar, R.; Sztaricskai, F.; Munk, M. E.; Tamas, J. *J. Org. Chem.* **1974**, *39*, 2971.

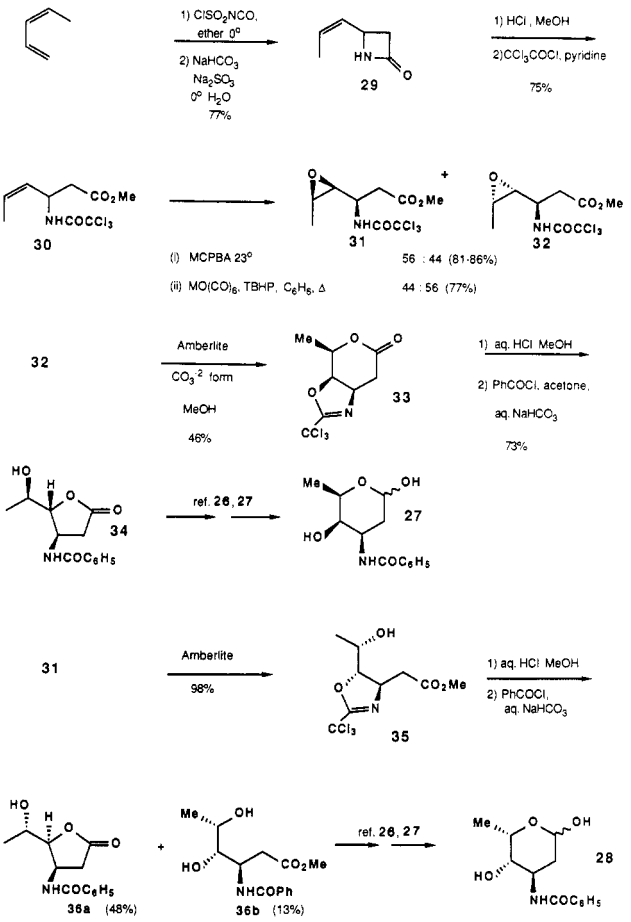
(20) (a) Penco, S. *Process Biochem.* **1980**, *15*, 12. (b) Remers, W. A. *The Chemistry of Antitumor Antibiotics*; Wiley-Interscience: New York, 1979; Chapter 2. (c) Arcamone, F.; Cassinelli, G.; Orezzi, P.; Francheschi, G.; Mondelli, R. *J. Am. Chem. Soc.* **1964**, *86*, 5335.

(21) Replacement of daunosamine in the parent antibiotics with acosamine (the arabino diastereomer) has led to less toxic analogues: (a) Arcamone, F.; Penco, S.; Vigevanti, A.; Redaelli, S.; Franchi, G.; DiMarco, A.; Casazza, A. M.; Dasdia, T.; Formelli, F.; Necco, A.; Soranzo, C. *J. Med. Chem.* **1975**, *18*, 703. (b) Arcamone, F.; Bargiotti, A.; Cassenelli, G.; Redaelli, S.; Hanessian, S.; DiMarco, A.; Casazza, A. M.; Dasdia, T.; Necco, A.; Reggiani, P.; Supino, R. *J. Med. Chem.* **1976**, *19*, 733.

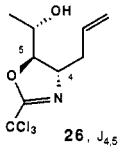
(22) For leading references to previous synthesis of ristosamine and acylated derivatives, see ref 9.

(23) Overman, L. E. *J. Am. Chem. Soc.* **1976**, *98*, 2901.

Scheme IV. Synthesis of Precursors to *N*-Benzoyldaunosamine (27) and *N*-Benzoyl-4-*epi*-ristosamine (28)



$J_{4,5}$ = 9 Hz observed in **24**. By way of comparison, oxazolidine **26** produced from the minor epoxide **23** showed



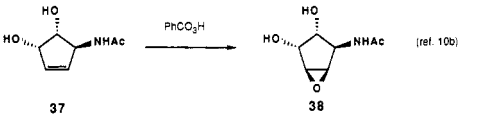
$J_{4,5}$ = 6 Hz. Finally, hydrolysis and benzoylation of **24** provided diol amide **25**,[24] which was then converted into a mixture of the pyranose (minor) and furanose (major) tautomers of *N*-benzoylristosamine by a standard ozonolytic sequence. The NMR data obtained for this mixture were in complete agreement with literature values.[26]

Synthesis of Precursors to *N*-Benzoyldaunosamine (27) and *N*-Benzoyl-4-*epi*-ristosamine (28). Encouraged by the results summarized in Table I for the $MO(CO)_6$-catalyzed epoxidation of **1a**, we decided to apply this reaction in a synthesis of *N*-benzoyldaunosamine (**27**).[27] Since the allyl unit of **21** had served as a source of competing reactions in the ristosamine synthesis, a different means of masking the aldehydic center in early daunosamine intermediates was sought. Taking the lead from Hauser's first synthesis of **27**,[27] the readily available azetidinone **29**[28] was selected as starting material (Scheme IV).

Acidic methanolysis of **29** followed by acylation of the intermediate amine hydrochloride with trichloroacetyl chloride gave amide **30** in 75% yield. To our surprise, the epoxidations of **30** using either peracids or the $Mo(CO_6)$–TBHB system were essentially nonstereoselective. Similar results were obtained with the C_6H_5CO and MeOCO derivatives. Stereostructural assignments in these cases were based on the conversion of **32** and **31** to the known[26,27] γ-lactones **34** and **36**, respectively. Because the stereoselectivity of the epoxidation step was so poor, no effort was made to complete syntheses of sugars **27** and **28**.

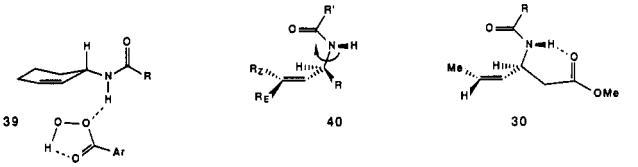
Discussion

At the outset we had anticipated that the peracid epoxidation of acyclic allylic amides would prove to be more highly stereoselective than the corresponding allylic alcohols. It was known, for example, that in cyclic systems an allylic amide is a stronger peracid directing group than an allylic alcohol (e.g., **37** → **38**).[10b] While our results show



that the peracid epoxidation of (*E*)-allylic amides **2a,b** and **21** (ca. 75:25) are slightly more threo-selective than analogous (*E*)-allylic alcohols (typically 65:35 in favor of the threo isomer), the same tendency is not apparent in the results with (*Z*)-allylic amides **1** and especially **30**.

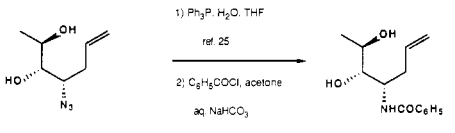
It is interesting to speculate that the superior performance of amides as directing groups in the epoxidation of cyclic vs. acyclic olefins may be related to the conformational preferences of these systems.[29] In a cyclic allylic amide such as **39** the amide NH will be in a favorable



position for hydrogen bonding to the peracid since (i) the s-trans conformation about the amide C–*N* bond is highly favored, and (ii) the amide carbonyl will nearly eclipse the N–C–H unit.[29] With acyclic allylic amides, however, the preferred orientation of the NH relative to the double bond is much different (see **40**), since the allylic C–H will preferentially remain in the plane of the olefin. The amide NH can direct epoxidation effectively in **40** only if rotation occurs about the allylic C–N bond such that the N–H is in a better position to serve as a hydrogen bond donor to the incoming peracid.

Two pieces of experimental evidence suggest that the orientation (and availability) of an NH is essential to achieving useful levels of stereoselection in this epoxidation

(24) The stereochemistry of **25** was confirmed by correlation with the known diol azide **i** (for preparation, see ref 8b). This, then, completes a second synthesis of *N*-benzoylristosamine from allylic alcohol **19**.



(25) Vaultier, M.; Knouzi, N.; Carrie, R. *Tetrahedron Lett.* **1983**, *24*, 763.

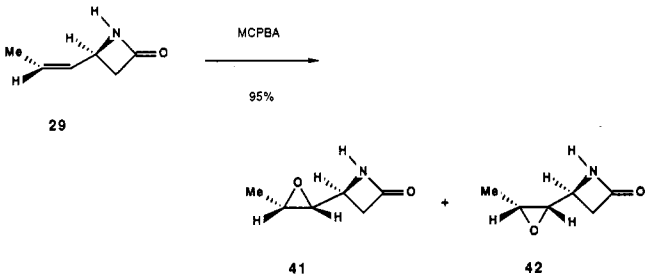
(26) Fronza, G.; Fuganti, C.; Grasselli, P. *J. Chem. Soc., Perkin Trans. 1* **1982**, 885.

(27) For previous syntheses of daunosamine, see ref 9a and Hauser, F. M.; Rhee, R. P.; Ellenberger, S. R. *J. Org. Chem.* **1984**, *49*, 2236.

(28) (a) Mariconi, E. J.; Meyer, W. C. *J. Org. Chem.* **1971**, *36*, 2841. (b) Goebel, P.; Claus, K. *Liebigs Ann. Chem.* **1969**, *722*, 122.

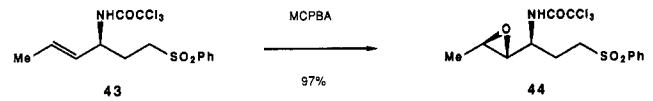
(29) (a) Doskocilova, D.; Schneider, B. *J. Mol. Struct.* **1976**, *31*, 337. (b) Schmidt, P.; Doskocilova, D.; Schneider, B. *Ibid.* **1973**, *15*, 383.

reaction. The first concerns the epoxidation of **30** (Scheme IV), which was found to occur with low stereoselection in favor of the erythro diastereomer **31**. This epoxidation substrate exists in solution with a strong intramolecular hydrogen bond between the NH and ester carbonyl (IR analysis), presumably precluding (or at least competing with) hydrogen bonding to the peracid.[30] The second concerns the epoxidation of azetidinone **29** in which the NH appears to be oriented properly to direct an epoxidation. In fact, treatment of **29** with MCPBA in CH_2Cl_2



at 23 °C provided an 82:18 mixture of **41** and **42**.[31] That the stereoselectivity was not higher probably suggests that the placement of the NH relative to the olefin still is not optimal.

Whether or not this interpretation is correct, our results certainly show that stereoselectivity in the epoxidation of acyclic allylic amides is substrate-dependent. This conclusion is strikingly emphasized by a recent report from Hauser's laboratory that the epoxidation of **43** provides **44** as a single diastereomer.[11c] Why the SO_2Ph substituent



plays such a major role in increasing the stereoselection relative to our ristosamine intermediate **21** (Scheme III) is not obvious at present. Care clearly must be exercised in selecting allylic amide substrates if this method is to prove useful in the synthesis of acyclic molecules.

Experimental Section

Proton (^1H) NMR spectra were measured in $CDCl_3$ at 250 MHz on a Bruker WM 250 instrument and at 300 MHz on a Varian XL-300 instrument. Chemical shifts are reported in δ units using the 7.24 ppm resonance of residual chloroform as internal reference. Infrared spectra were measured on Perkin-Elmer Model 238B or 237 B infrared spectrophotometers calibrated with the 1601 cm^{-1} absorption of polystyrene. IR spectra are reported in wavenumbers (cm^{-1}). Mass spectra were measured at 70 eV on a Varian MAT 44 or a Finnegan MAT 8200 instrument. High-resolution mass spectra were measured at 70 eV on the Finnegan MAT 8200. Elemental analyses were performed by Robertson Laboratory, Inc., Florham Park, NJ.

All reactions were conducted in oven-dried (125 °C) or flame-dried glassware under atmospheres of dry argon or nitrogen. All solvents were purified before use. Ether, THF, benzene, and toluene were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from CaH_2. Hexane was distilled from NaH.

Analytical thin-layer chromatography (TLC) was performed by using 2.5 cm × 10 cm plates coated with a 0.25-mm thickness of silica gel containing PF 254 indicator (Analtech). Preparative thin-layer chromatography (PTLC) was performed by using 20 cm × 20 cm plates coated with 0.25- or 0.5-mm thicknesses of silica gel containing PF 254 indicator (Analtech). Compounds were visualized by charring with ethanolic vanillin/H_2SO_4 or by staining with iodine vapor. Compounds were eluted from the adsorbents with ether or ethyl acetate. Column chromatography was performed on Woelm 230–400- or 70–230-mesh silica gel (Merck). Radial chromatography was performed on a Harrison Research chromatotron Model 7924 using 24-cm diameter plates coated with 1-mm thickness of silica gel containing PF 254 indicator (Merck). All chromatography solvents were distilled prior to use.

1-Phenylpent-3-yn-2-ol (10). To a solution of *n*-butyllithium (2.6 mL of 3.3 M solution in hexane, 8.6 mmol) in 60 mL of THF at −78 °C was added approximately 5 mL of propyne (dried by passing through $CaCl_2$ and Dehydrite). The mixture was stirred for 30 min and then phenylacetyladehyde (1 mL, 8.1 mmol) was added. The reaction mixture was stirred for 2 h with gradual warming to −20 °C and then was quenched by the addition of 10 mL of MeOH. The resulting yellow solution was washed with 15 mL of 1 N HCl and then 10 mL of water. The combined aqueous phases were extracted with 3 × 15 mL of CH_2Cl_2. The extracts were dried (Na_2SO_4), filtered, and concentrated to yield 1.48 g of crude product. This material was distilled (Kugelrohr, 107 °C, 1 mm) to give 1.15 g (88% yield) of **10** that was sufficiently pure for use in succeeding reactions. An analytical sample purified by preparative TLC (1:1 ether–hexane, R_f 0.59): ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 4.5 (t, J = 6.5 Hz, 1 H, H_2), 2.9 (m, 2 H, H_1), 2.3 (br, 1 H, OH), 1.79 (d, J = 2.0 Hz, 3 H, H_5); IR (neat) 3100–3600 (br OH), 3030, 2920, 2235, 1605, 1495, 1455, 1030, 695 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.53; H, 7.78.

1-Phenyl-2-aminopent-3-yne (11). To a solution of 1.5 g (9.4 mmol) of **10**, 2.66 g (10.2 mmol) of triphenylphosphine, and 1.53 g (10.4 mmol) of phthalimide in 75 mL of dry THF was added 1.8 mL (11.4 mmol) of diethyl azodicarboxylate. The resulting yellow solution was stirred at 23 °C for 20 h. The solvent was removed in vacuo to afford 8.9 g of semisolid material, which was taken up in 1:1 ether–hexane. The resulting precipitate was triturated with several portions of 1:1 ether–hexane. Concentration of the filtrate afforded 6 g of yellow oil. This material was purified by flash chromatography to yield 2.88 g of solid material, which was recrystallized from ether–hexane to yield 1.66 g (61%) of pure 1-phenyl-2-phthalimidopent-3-yne, mp 96–97 °C: ^1H NMR ($CDCl_3$) δ 7.77 (dd, J = 3.2, 5.3 Hz, 2 H), 7.65 (dd, J = 3.2, 5.3 Hz, 2 H), 7.17 (s, 5 H, phenyl), 5.21 (m, 1 H, H_2), 3.41 (dd, J = 9.2, 13.6 Hz, 1 H, H_{1a}), 3.32 (dd, J = 7.2, 13.6 Hz, 1 H, H_{1b}), 1.80 (d, J = 2.0 Hz, 3 H, H_5); IR (CH_2Cl_2) 3050, 2930, 2240, 1780, 1720, 1495, 1470, 1385, 1350, 1100 cm^{-1}; mass spectrum, m/e 289 (parent ion).

A solution of 1.53 g (5.28 mmol) of the above phthalimide and 0.3 mL (6.18 mmol) of hydrazine hydrate in 45 mL of absolute EtOH was heated to reflux for 3.5 h, resulting in the formation of a white precipitate. The reaction mixture was cooled to 23 °C and 6 mL of concentrated HCl was added. The precipitate was removed by filtration and the filtrate was concentrated to a solid residue. This material was dissolved in 60 mL of 2:1 EtOH–H_2O. The insoluble portion was removed and the filtrate was brought to pH >10 by the addition of 1 N NaOH. The solution was extracted with 7 × 30 mL of Et_2O. The combined extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo to afford 820 mg of crude **11**. Bulb-to-bulb distillation (110 °C, 0.7 mm) afforded 708 mg (84% yield) of **11** as a slightly colored liquid: ^1H NMR ($CDCl_3$) δ 7.2–7.3 (m, 5 H, aromatic), 3.75 (m, 1 H, H_2), 2.92 (dd, J = 6.0, 13.2 Hz, 1 H, H_{1a}), 2.77 (dd, J = 7.2, 13.2 Hz, 1 H, H_{1b}), 1.78 (d, J = 2.0 Hz, 3 H, H_5), 1.47 (br, 2 H, NH_2); IR (neat) 3100–3700 (br NH_2), 3030, 2920, 2220, 1605, 1495, 1455, 695 cm^{-1}; mass spectrum, m/e 159 (parent ion).

(*Z*)-1-Phenyl-2-aminopent-3-ene (7). A suspension of 481 mg of **11** and 26 mg of Lindlar catalyst in 25 mL of absolute MeOH was stirred vigorously under 1 atm of H_2. After 110 min, GC analysis (9 ft 5% SE-30 on Chrom G, 52 psi, 150 °C) showed no **11** (t_R 4.4 min) and a new peak corresponding to **7** (t_R 3.4 min). The catalyst was removed by filtration through a Celite pad and the solvent was removed in vacuo to yield 487 mg (95% yield) of **7**: ^1H NMR ($CDCl_3$) δ 7.2–7.3 (m, 5 H, aromatic), 5.5 (dq, J

(30) Stereoselectivity also dropped significantly in the $Mo(CO)_6$-catalyzed epoxidation of **30**. While it is easy to suggest that the CO_2Me group interacts with the catalytically active Mo species, it is not obvious how such an interaction would adversely affect the stereoselectivity.

(31) (a) We assume that the major product of this reaction is the threo diastereomer **41**. Thus far we have been unsuccessful in attempts to manipulate the azetidinone in route to useful daunosamine precursors. (b) The $Mo(CO)_6$-catalyzed epoxidation of **29** provided **41** and **42** in a ratio of 79:21.

= 6.7, 17.4 Hz, 1 H, H_4), 5.35 (ddd, J = 1.4, 7, 17.4 Hz, 1 H, H_3), 3.93 (br q, J = 7 Hz, 1 H, H_2), 2.7 (d, J = 6.8 Hz, 2 H, H_1), 1.49 (dd, J = 1.4, 6.7 Hz, 3 H, H_5); IR (neat) 3100–3700 (br NH_2), 3020, 2920, 1650, 1600, 1495, 1455, 695 cm^{-1}.

(*E*)-1-Phenylpent-2-en-4-ol (12). A suspension of 2.39 g (19.9 mmol) of phenylacetaldehyde and 7 g (22 mmol) of 1-(triphenylphosphoranylidene)-2-propanone in 250 mL of dry THF was stirred at 0 °C for 135 h. The solvent was removed in vacuo and the solid residue was triturated with several portions of hexane. The extracts were evaporated, and the crude product was purified by flash chromatography (230 g of silica gel with 7:3 hexane–ether as eluant) to yield 2.83 g (89%) of (*E*)-1-phenylpent-2-en-4-one: ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 6.96 (dt, J = 6.8, 16.0 Hz, 1 H, H_2), 6.12 (dm, J = 16.0 Hz, 1 H, H_3), 3.59 (br d, J = 6.8 Hz, 2 H, H_1), 2.29 (s, 3 H, H_5); IR (CH_2Cl_2) 3030, 2920, 1670, 1625, 1605, 1495, 1450, 1360, 980 cm^{-1}; mass spectrum, m/e 160 (parent ion).

A solution of 2.67 g (16.7 mmol) of the above enone in 150 mL of dry Et_2O was cooled to −78 °C and 19 mL of 1 M DIBAL in hexane was added. After 30 min, the reaction mixture was brought to 23 °C and stirred for 1 h. The reaction was quenched by the addition of 30 mL of MeOH. Then, just enough 6 N HCl was added to dissolve the precipitate that had formed. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were dried (Na_2SO_4), filtered, and concentrated to afford 2.57 g (95% yield) of **12**: ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 5.82 (ddt, J = 0.9, 6.8, 15.2 Hz, 1 H, H_2), 5.61 (ddt, J = 1.3, 6.4, 15.2 Hz, 1 H, H_3), 4.29 (quintet, J = 6.4 Hz, 1 H, H_4), 3.40 (br d, J = 6.8 Hz, 2 H, H_1), 2.06 (br, 1 H, OH), 1.30 (d, J = 6.4 Hz, 3 H, H_5); IR (CH_2Cl_2) 3100–3600 (br OH), 3030, 2970, 1670, 1605, 1495, 1450, 1060, 970, 695 cm^{-1}; mass spectrum, m/e 162 (parent ion).

***N*-((*E*)-1-Phenylpent-3-en-2-yl)trichloroacetamide (2a).** A solution of 2.34 g (14.4 mmol) of **12** in 16 mL of dry THF was treated with approximately 110 mg of KH (prepared from 310 mg of 35% KH in mineral oil by washing 3× with hexane). After 5 min, the dark orange solution was transferred by cannula into a 0 °C solution of 1.6 mL (16 mmol) of trichloroacetonitrile in 16 mL of dry Et_2O. The reaction mixture was maintained at 0 °C for 1.5 h and then warmed to 23 °C over 1 h. The solvent was removed and the residue was taken up in 60 mL of pentane and 0.16 mL of MeOH. The mixture was stirred vigorously for 10 min and the precipitate was removed by filtration. The solvent was evaporated to afford 4.14 g (94% yield) of the intermediate imidate ester as a golden liquid: ^1H NMR ($CDCl_3$) δ 8.29 (br, 1 H, NH), 7.2–7.4 (m, 5 H, aromatic), 5.97 (ddt, J = 0.8, 6.8, 15.2 Hz, 1 H, H_2), 5.65 (ddt, J = 1.4, 6.3, 15.2 Hz, 1 H, H_3), 5.51 (quintet, J = 6.3 Hz, 1 H, H_4), 3.40 (d, J = 6.8 Hz, 2 H, H_1), 1.44 (d, J = 6.3 Hz, 3 H, H_5); IR (neat) 3340, 3030, 2980, 1660, 1605, 1495, 1450, 1285, 1080, 965, 695, 645 cm^{-1}; mass spectrum, m/e 305, 306, 307, 308 (parent ions).

A solution of 943 mg (3.1 mmol) of the above imidate ester in 10 mL of xylene was heated to reflux for 8 h. After being cooled to 23 °C, the brown solution was filtered through 7 g of silica gel by using toluene as the eluant. After removal of the solvents in vacuo, the crude product was distilled (Kugelrohr, 160–165 °C, 1.1 mm) to yield 771 mg (82% yield) of slightly colored liquid which solidified on cooling. The solid was recrystallized from hexane to afford 676 mg (72% yield) of **2a** as white needles: mp 73–74 °C: ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 6.50 (br, 1 H, NH), 5.63 (ddq, J = 0.9 Hz, 6.4, 15.2 Hz, 1 H, H_4), 5.41 (ddq, J = 1.4, 6.2, 15.2 Hz, 1 H, H_3), 4.62 (m, 1 H, H_2), 2.96 (dd, J = 6.4, 13.7 Hz, 1 H, H_{1a}), 2.87 (dd, J = 6.5, 13.7 Hz, 1 H, H_{1b}), 1.67 (dm, J = 6.4 Hz, 3 H, H_5); IR (CH_2Cl_2) 3410, 3040, 2920, 1715, 1505, 1440, 1245, 965, 815 cm^{-1}; mass spectrum, m/e 305, 306, 307, 308 (parent ions). Anal. Calcd for $C_{13}H_{14}Cl_3NO$: C, 50.92; H, 4.60; N, 4.57. Found: C, 51.02; H, 4.70; N, 4.77.

(*E*)-1-Phenyl-2-aminopent-3-ene (8). A solution of 1.06 g (3.44 mmol) of **2a** in 16 mL of EtOH was treated with 20 mL of 5 N NaOH for 3 h (23 °C). The reaction mixture was diluted with 30 mL of Et_2O and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (4 × 20 mL). The combined extracts were dried (Na_2CO_3), filtered, and concentrated in vacuo to afford 505 mg of viscous oil. This material was distilled (Kugelrohr) at 90–95 °C (1.0 mm) to give 344 mg (62% yield) of colorless **8**: ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 5.45–5.66 (m, 2 H, H_3 and H_4), 3.6 (m, 1 H, H_2), 2.83 (dd, J = 5.1, 13.3 Hz, 1 H, H_{1a}), 2.59 (dd, J = 8.4, 13.3 Hz, 1 H, H_{1b}), 1.70 (d, J = 5.3, 3 H, H_5).

***N*-((*Z*)-1-Phenylpent-3-en-2-yl)trichloroacetamide (1a).** Trichloroacetyl chloride (0.150 mL, 1.34 mmol) was added to a solution of **7** (100 mg, 0.62 mmol) in 1 mL of dry pyridine and 9 mL of dry CH_2Cl_2. The mixture was stirred at 23 °C for 19 h and then was quenched with water (11 mL). This mixture was stirred for 10 min, then was diluted with CH_2Cl_2 (10 mL), and extracted with aqueous HCl (1 N, 2 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated to yield 248 mg of brown liquid. This was filtered through silica gel with 1:1 ether–hexane and recrystallized from ether–hexane to give 99 mg (52%) of **1a** as a white solid, mp 64–67 °C, and 74 mg of mother liquor. This material was chromatographed (0.5 mm silica gel preparative plate, 1:1 ether–hexane) to give an additional 55 mg (29%) of **1a** as a white solid: ^1H NMR ($CDCl_3$) δ 7.27 (m, aromatic), 6.57 (br d, J = 2.5 Hz, 1 H, NH), 5.66 (dq, J = 9, 7 Hz, 1 H, H_4), 5.33 (ddq, J = 7, 9, 2 Hz, 1 H, H_3), 4.93 (m, 1 H, H_2), 3.00 (dd, J = 13.5, 7 Hz, 1 H, H_{1a}), 2.90 (dd, J = 7, 13.5 Hz, 1 H, H_{1b}), 1.60 (dd, J = 1.8, 7 Hz, 3 H H_5); IR ($CHCl_3$) 3425, 2920, 1710, 1492 cm^{-1}; mass spectrum, m/e 307, 306, 305 (parent ions). Anal. Calcd for $C_{13}H_{14}NOCl_3$: C, 50.92; H, 4.60; N, 4.57. Found: C, 50.86; H, 4.67; N, 4.63.

***N*-((*Z*)-1-Phenylpent-3-en-2-yl)benzamide (1b).** A solution of 45 mg (0.38 mmol) of **7** in 4 mL of CH_2Cl_2 and 0.4 mL of pyridine was treated with 0.065 mL (0.56 mmol) of benzoyl chloride. After 14 h, the reaction was worked up as described for **1a**. The crude product was chromatographed on a 0.5 mm silica gel plate (2:1 hexane/ether, 2 developments, R_f 0.5) and then recrystallized from ether–hexane to yield 53 mg (72% yield) of **1b** as fine needles, mp 100.5–101.5 °C: ^1H NMR ($CDCl_3$) δ 7.2–7.7 (m, 10 H, aromatic), 6.0 (br d, J = 10 Hz, 1 H, NH), 5.58 (dq, J = 6.7, 10.6 Hz, 1 H, H_4), 5.33 (ddq, J = 1.6, 9.0, 10.6 Hz, 1 H, H_3), 5.16 (m, 1 H, H_2), 3.03 (dd, J = 5.2, 13.3 Hz, 1 H, H_{1a}), 2.88 (dd, J = 7.3, 13.3 Hz, 1 H, H_{1b}), 1.57 (dd, J = 1.6, 6.7 Hz, 3 H, H_5); IR (CH_2Cl_2) 3440, 3050, 3030, 2920, 1660, 1603, 1580, 1505, 1480, 1255 cm^{-1}; mass spectrum, m/e 265 (parent ion).

***N*-Carbomethoxy-(*Z*)-1-phenyl-2-aminopent-3-ene (1c).** A solution of 112 mg (0.7 mmol) of **7** in 9 mL of CH_2Cl_2 and 1 mL of pyridine was treated with 0.06 mL (0.8 mmol) of methyl chloroformate. After 14 h, the reaction was worked up by using the method described for the preparation of **1a**. Crude **1c** was chromatographed on a 0.5 mm silica gel plate using 1:1 hexane–ether as the eluant to afford 143 mg of material (R_f 0.46). Further purification by Kugelrohr distillation at 140 °C (1 mm) provided 127 mg (83% yield) of pure **1c**: ^1H NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H, aromatic), 5.57 (dq, J = 6.9, 10.7 Hz, 1 H, H_4), 5.28 (ddq, J = 1.6, 9, 10.7 Hz, 1 H, H_3), 4.72 (br, 2 H, H_2 and NH), 3.69 (s, 3 H, OCH_3), 2.8 (m, 2 H, H_1), 1.55 (dd, J = 1.6, 6.9 Hz, 3 H, H_5); IR (neat) 3420, 3030, 2920, 1715, 1605, 1510, 1220, 965, 820 cm^{-1}; mass spectrum, m/e 219 (parent ion). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.34; H, 8.04; N, 6.41.

***N*-((*Z*)-1-Phenylpent-3-en-2-yl)-*N'*-phenylurea (1d).** A solution of 135 mg (0.84 mmol) of **7** in 4 mL of CH_2Cl_2 and 1 mL of pyridine was treated with 0.125 mL (1.24 mmol) of phenyl isocyanate. After 13 h, 1 mL of MeOH was added and the mixture was stirred for 1.5 h. The solvent was removed, and the resulting crude product was partially purified by flash chromatography on 100 g of silica gel using 1:1 hexane/ether as the eluant. This afforded 276 mg of viscous oil. Recrystallization from ether–CCl_4 afforded 238 mg of amorphous solid (>95% yield) which was used in subsequent steps without further purification: ^1H NMR ($CDCl_3$) δ 7.0–7.7 (m, 10 H, aromatic), 6.75 (br, 1 H, NH), 5.50 (dq, J = 6.9, 10.7 Hz, 1 H, H_4), 5.20 (ddq, J = 1.6, 9.1, 10.7 Hz, 1 H, H_3), 5.02 (br d, J = 7.1 Hz, 1 H, NH), 4.80 (br quintet, J = 7 Hz, H_2), 2.88 (dd, J = 5.9, 13.3 Hz, 1 H, H_{1a}), 2.71 (dd, J = 7.3, 13.3 Hz, 1 H, H_{1b}), 1.49 (dd, J = 1.6, 6.9 Hz, 3 H, H_5); IR (CH_2Cl_2) 3100–3400 (br NH), 3040, 2980, 1670, 1600, 1520, 1495, 1250, 890 cm^{-1}.

***N*-Carbomethoxy-(*E*)-1-phenyl-2-aminopent-3-ene (2b).** A solution of 161 mg (1.0 mmol) of **8** in 10 mL of CH_2Cl_2 and 1 mL of pyridine was treated with 0.1 mL (1.3 mmol) of methyl chloroformate. After 15 h, the reaction was worked up using the procedure described for **1a**. Partial purification of the crude product by flash chromatography on 28 g of silica gel (2:1 hexane/ether as eluant) afforded 210 mg colorless oil, which was

distilled (125–130 °C (0.7 mm), Kugelrohr) to yield 196 mg (89%) of **2b**, mp <35 °C: ^{1}H NMR ($CDCl_3$) δ 7.2–7.3 (m, 5 H, aromatic), 5.55 (dq, J = 6.4, 15.4 Hz, 1 H, H_4), 5.36 (dd, J = 5.8, 15.4 Hz, 1 H, H_3), 4.57 (br, 1 H, NH), 4.37 (br m, 1 H, H_2), 3.60 (s, 3 H, OCH_3), 2.80 (br d, J = 6.5 Hz, 2 H, H_1), 1.63 (d, J = 6.4 Hz, 3 H, H_5); IR (CH_2Cl_2) 3430, 3030, 2940, 1720, 1605, 1505, 1440, 1350, 1250, 965, 890 cm^{-1}.

***N*-((*E*)-1-Phenylpent-3-en-2-yl)-*N'*-phenylurea (2c).** A solution of 125 mg (0.78 mmol) of **8** in 9 mL of CH_2Cl_2 and 1 mL of pyridine was treated with 0.1 mL (0.95 mmol) of phenyl isocyanate by using the procedure described for the preparation of **1d**. The crude product was chromatographed on 100 g of flash silica gel (2:1 hexane/ether as eluant) to yield 264 mg of thick oil. This material was crystallized from ether–hexane to yield 138 mg (64% yield) of **2c** as white needles, mp 50–55 °C: ^{1}H NMR ($CDCl_3$) δ 7.94 (br, 1 H, NH), 7.0–7.4 (m, 10 H, aromatic), 6.00 (br d, J = 8 Hz, 1 H, NH), 5.54 (dq, J = 6.1, 15.4 Hz, 1 H, H_4), 5.35 (dd, J = 5.3, 15.4 Hz, 1 H, H_3), 4.55 (br quintet, J = 7 Hz, 1 H, H_2), 2.73 (d, J = 7 Hz, 2 H, H_1), 1.60 (d, J = 6.1 Hz, 3 H, H_5); IR (CH_2Cl_2) 3100–3400 (br NH), 3040, 2980, 1670, 1600, 1570, 1545, 1250, 965, 890 cm^{-1}.

Representative Procedure for Peracid Epoxidation. A solution of 58.9 mg (0.192 mmol) of **1a** in 3 mL of dry CH_2Cl_2 was treated with 100 mg (0.58 mmol) of MCPBA at 23 °C. The reaction mixture was stirred for 5 h, then was diluted with 50 mL of CH_2Cl_2, and washed with saturated aqueous $NaHSO_3$ (2 × 30 mL) and saturated aqueous $NaHCO_3$ (30 mL). The combined aqueous extracts were back-extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phases were dried over Na_2SO_4 and filtered. The solvent was evaporated in vacuo to afford 66.6 mg of a white solid which proved to be a 75:25 mixture of epoxides **3a** and **4a** (NMR analysis). Separation of this mixture by chromatography (silica gel, 4:1 hexane–ether) afforded 46 mg (74%) of **3a** (arabino) and 7 mg (11%) of the ribo diastereomer **4a**.

Representative Procedure for $Mo(CO)_6$/TBHP Epoxidations. A solution of 168 mg (0.55 mmol) of **1a**, 1.2 mL of TBHP (3.0 M in CH_2Cl_2, 3.6 mmol), and 20 mg (0.076 mmol) of $Mo(CO)_6$ in 10 mL of benzene was heated in an 84 °C oil bath for 3.5 h. Since the reaction had not gone to completion, another 3 mg (0.01 mmol) of $Mo(CO)_6$ was added and the mixture heated for another 0.5 h. The solution was then filtered through silica gel by using ethyl acetate as eluant. The solvent was removed in vacuo to afford 165 mg of crude product. High-field NMR analysis revealed this material to be a 9:79:3:9 mixture of **1a**, **3a**, **4a**, and **14a** resulting from intramolecular opening of ribo epoxide **4a**. The kinetic selectivity of this reaction, therefore, was 87:13 in favor of arabino epoxide **3a**. This material was chromatographed (silica gel, 1:1 ether–hexane) to afford 13 mg (8%) of recovered **1a**, 107 mg (60%) of **3a**, and 23 mg (13%) of **14a**.

***N*-(*arabino*-3,4-Epoxy-1-phenylpent-2-yl)trichloroacetamide (3a)**: mp 133–137 °C; ^{1}H NMR ($CDCl_3$) δ 7.31 (m, aromatic), 6.88 (br d, J = 6.5 Hz, 1 H, NH), 3.95 (m, 1 H, H_2), 3.16 (dd, J = 5, 13.5 Hz, 1 H, H_{1a}), 3.05 (m, 2 H, H_3, H_4), 2.91 (dd, J = 8.3, 13.5 Hz, 1 H, H_{1b}), 1.01 (d, J = 5.3 Hz, 3 H, H_5); IR ($CHCl_3$) 3422, 3005, 1714, 1500 cm^{-1}; mass spectrum, m/e 322, 324 (M^+ + 1). Anal. Calcd for $C_{13}H_{14}NO_2Cl_3$: C, 48.40; H, 4.37; N, 4.34. Found: C, 48.20; H, 4.47; N, 4.14.

***N*-(*arabino*-3,4-Epoxy-1-phenylpent-2-yl)benzamide (3b)**: mp 159–163 °C; R_f 0.33 (1:1 ether/hexane, 3 developments); ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 7 Hz, 2 H, aromatic), 7.43 (m, 3 H, aromatic), 7.28 (m, 5 H, aromatic), 6.49 (d, J = 7 Hz, 1 H, NH), 4.19 (m, 1 H, H_2), 3.24 (dd, J = 5, 13 Hz, 1 H, H_3), 3.07 (m, 2 H, H_4), 2.90 (dd, J = 9, 13 Hz, 1 H, H_1), 0.96 (d, J = 6 Hz, 3 H, H_5); IR (CH_2Cl_2) 3440, 2940, 1660, 1510, 1485 cm^{-1}; mass spectrum, m/e 281 (parent ion); high resolution mass spectrum for $C_{18}H_{19}NO_2$, calcd 281.1416, found 281.1415.

***N*-Carbomethoxy-*arabino*-2-amino-3,4-epoxy-1-phenylpentane (3c)**: mp 105–108 °C; R_f 0.22 (1:1 ether/hexane); ^{1}H NMR ($CDCl_3$) δ 7.18 (m, 5 H, aromatic), 5.08 (br s, 1 H, NH), 3.61 (s and m, 4 H, OCH_3 and H_2), 3.04 (m, 1 H), 2.91 (m, 2 H), 2.74 (dd, J = 9, 13 Hz, 1 H), 0.84 (d, J = 6 Hz, 3 H, H_5); IR (CH_2Cl_2) 3440, 2960, 1720, 1505, 1225, 1031 cm^{-1}); mass spectrum, m/e 191 (no parent ion observed). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.60; H, 7.20; N, 5.97.

***N*-(*arabino*-3,4-Epoxy-1-phenylpent-2-yl)-*N'*-phenylurea (3d)**: ^{1}H NMR (d_6-acetone) δ 7.88 (br s, 1 H, NH), 7.43 (d, J = 8 Hz, 2 H, aromatic), 7.25 (d, J = 4 Hz, 4 H, aromatic), 7.17 (m, 3 H, aromatic), 6.86 (t, J = 7 Hz, 1 H, aromatic), 5.93 (d, J = 7 Hz, 1 H, NH), 3.79 (m, 1 H, H_2), 3.06 (dd, J = 6, 13 Hz, 1 H, H_1), 2.90 (m, 3 H), 0.80 (d, J = 6 Hz, 3 H, H_5); IR (CH_2Cl_2) 3420, 3320, 3025, 2980, 1680, 1600, 1520, 1250 cm^{-1}; mass spectrum, m/e 296 (parent ion). Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 73.11; H, 6.95; N, 9.52.

***N*-(*ribo*-3,4-Epoxy-1-phenylpent-2-yl)trichloroacetamide (4a)**: ^{1}H NMR δ 7.26 (m, aromatic), 6.55 (br d, J = 6.5 Hz, 1 H, NH), 3.91 (m, 1 H, H_2), 3.17 (dq, J = 4, 5.5 Hz, 1 H, H_4), 3.14 (dd, J = 3.6, 14.6 Hz, 1 H, H_{1a}), 3.04 (dd, J = 6.7, 14.1 Hz, 1 H, H_{1b}), 2.84 (dd, J = 4.8 Hz, 1 H, H_3), 1.43 (d, J = 5.5 Hz, 3 H, H_5); IR ($CHCl_3$) 3420, 2970, 1717, 1500, 1460 cm^{-1}; mass spectrum, m/e 322, 324 (M^+ + 1).

***N*-Carbomethoxy-*ribo*-2-amino-3,4-epoxy-1-phenylpentane (4c)**: R_f 0.28 (1:1 ether–hexane); ^{1}H NMR ($CDCl_3$) δ 7.28 (m, aromatic), 4.60 (br s, 1 H, NH), 3.75 (br m, 1 H, H_2), 3.63 (s, 3 H, OCH_3), 3.18 (dq, J = 5, 5 Hz, 1 H, H_4), 3.09 (dd, J = 4, 13 Hz, 1 H, H_3), 2.94 (br dd, J = 6, 13 Hz, 1 H), 2.78 (dd, J = 4, 8 Hz, 1 H, H_3), 1.45 (d, J = 5 Hz, 3 H, H_5); IR (CH_2Cl_2) 3440, 2960, 1725, 1510, 1360, 1225, 1085, 1045 cm^{-1}; mass spectrum, m/e 235 (parent ion); high resolution mass spectrum for $C_{13}H_{17}NO_3$, calcd 235.1209, found 235.1205.

***N*-(*xylo*-3,4-Epoxy-1-phenylpent-2-yl)trichloroacetamide (5a)**: mp 80 °C; R_f 0.36 (1:1 ether–hexane); ^{1}H NMR ($CDCl_3$) δ 7.24 (m, 5 H, aromatic), 6.59 (d, J = 7 Hz, 1 H, NH), 4.36 (m, 1 H, H_2), 2.99 (d, J = 6.5 Hz, 1 H, H_{1a}), 2.96 (d, J = 7 Hz, 1 H, H_{1b}), 2.82 (m, 2 H, H_3, H_4), 1.23 (d, J = 5 Hz, 3 H, H_5); IR (CH_2Cl_2) 3415, 2990, 1720, 1510, 1250, 820 cm^{-1}; mass spectrum, m/e 321 (parent ion). Anal. Calcd for $C_{13}H_{14}NO_2Cl_3$: C, 48.40; H, 4.37; N, 4.34. Found: C, 48.35; H, 4.35; N, 4.43.

***N*-Carbomethoxy-*xylo*-2-amino-3,4-epoxy-1-phenylpentane (5b) and *N*-carbomethoxy-*lyxo*-2-amino-3,4-epoxy-1-phenylpentane (6b)** prepared from the epoxidation of **2b** were not separable by chromatography. NMR resonances assigned to **5b**: ^{1}H NMR ($CDCl_3$) δ 7.22 (m, aromatic), 4.90 (br m, 1 H, NH), 4.05 (br m, 1 H, H_2), 3.58 (s, 3 H, OCH_3), 3.0–2.6 (complex multiplet, unresolved diastereomeric protons, 4 H, H_1, H_3, H_4), 1.18 (d, J = 3.5 Hz, 3 H, H_5). ^{1}H resonances assigned to **6b**: 3.72 (br m, 1 H, H_2), 3.57 (s, 3 H, OCH_3), 1.26 (d, J = 6 Hz, 3 H, H_5); IR (CH_2Cl_2; diasteromer mixture) 3430, 2960, 1725, 1510, 1440, 1350, 1220, 1070, 1025, 855 cm^{-1}; mass spectrum of diastereomer mixture, m/e 236 (parent ion + H); high resolution mass spectrum for $C_6H_{10}NO_3$ (p-$C_6H_5CH_2$), calcd 144.0661, found 144.0660.

***N*-(*xylo*-3,4-Epoxy-1-phenylpent-2-yl)-*N'*-phenylurea (5c)**: mp 185–188 °C (recrystallized from acetone–hexane); R_f 0.5 (4:1 hexane–acetone, 5 developments); ^{1}H NMR (acetone-d_6) δ 8.07 (br s, 1 H, NH), 7.47 (d, J = 8 Hz, 2 H), 7.39 (d, J = 8 Hz, 1 H), 7.20 (m, 5 H), 6.91 (m, 2 H), 5.63 (d, J = 9 Hz, 1 H, NH), 4.13 (m, 1 H, H_2), 2.89 (dd, J = 8, 14 Hz, 1 H, H_{1a}), 2.83 (dd, J = 8, 14 Hz, 1 H, H_{1b}), 2.70 (m, 2 H, H_3, H_4), 1.09 (d, J = 5 Hz, 3 H, H_5); IR ($CHCl_3$) 3425, 3325, 3000, 1670, 1595, 1520, 1490, 1440, 1305, 1200 cm^{-1}; mass spectrum, m/e 296 (parent ion); high resolution mass spectrum for $C_{18}H_{20}N_2O_2$, calcd 296.1525, found 296.1525.

***N*-(*lyxo*-3,4-Epoxy-1-phenylpent-2-yl)trichloroacetamide (6a)**: R_f 0.29 (1:1 ether–hexane); ^{1}H NMR ($CDCl_3$) δ 7.27 (m, 5 H, aromatic), 6.59 (d, J = 6 Hz, 1 H, NH), 4.01 (m, 1 H, H_2), 3.15 (m, 2 H, H_{1a}, H_4), 2.94 (d, J = 7.3, 14.1 Hz, 1 H, H_{1b}), 2.73 (dd, J = 6, 2 Hz, 1 H, H_3), 1.28 (d, J = 5 Hz, 3 H, H_5); IR (CH_2Cl_2) 3420, 2990, 1720, 1510, 1250, 820 cm^{-1}; mass spectrum, m/e 321 (parent ion).

Representative Procedure for the Intramolecular Opening of Epoxides. A mixture of ribo epoxide **4a** (5 mg, 0.16 mmol) and Amberlite resin (0.05 mL in MeOH, IRA-400 washed with saturated aqueous Na_2CO_3) was heated in 1 mL of MeOH at reflux for 3 h. The resin was filtered off and rinsed with MeOH, and the filtrate was evaporated in vacuo to give 4.6 mg (92%) of pure [4(*R**,*S**),5(*S**,*R**)-*trans*]-2-(trichloromethyl)-4-benzyl-5-[1-(*R**,*S**)-hydroxyethyl]-2-oxazoline (**14a**): ^{1}H NMR ($CDCl_3$) δ 7.26 (m, aromatic), 4.36 (m, 1 H, H_4), 4.34 (m, 1 H, H_5), 3.55 (m, 1 H), 3.18 (dd, J = 4.5, 13.8 Hz, 1 H), 2.79 (dd, J = 8, 13.6 Hz, 1 H), 0.98 (d, J = 6.6 Hz, 3 H); when the resonance at δ 0.98 was irradiated, δ 3.55 collapsed to a doublet, J = 4.5 Hz; IR ($CHCl_3$) 3605, 2960, 1670, 1455, 1385 cm^{-1}; mass spectrum, m/e 321, 323 (parent ions); high resolution mass spectrum for $C_{13}H_{14}NO_2Cl_3$,

calcd 321.0090, found 321.0091.

The stereochemistry of **14a** was assigned after acetylation. Thus, a sample of **14a** (2.7 mg (0.008 mmol)) was treated with Ac_2O (0.01 mL, 0.11 mmol) and DMAP (0.5 mg, 0.004 mmol) in 0.1 mL of pyridine at 23 °C for 28 h. The solvent was evaporated in vacuo, and the crude material was chromatographed (0.25 mm silica gel preparative plate, 4:1 hexane–ether) to afford 3 mg of acetate derivative: ^{1}H NMR ($CDCl_3$) δ 7.25 (m, aromatic), 4.83 (m, 1 H, H_4), 4.56 (dd, J = 5, 5 Hz, 1 H, H_5), 4.31 (m, 1 H), 3.15 (dd, J = 14, 5 Hz, 1 H), 2.74 (dd, J = 14, 8 Hz, 1 H), 1.89 (s, OAc), 1.12 (d, J = 6.5 Hz, 3 H); when the signal at δ 4.83 was irradiated, the peak at δ 4.56 collapsed to a doublet, J = 5 Hz, and the signal at δ 1.12 collapsed to a singlet; IR ($CHCl_3$) 2880, 1745, 1645, 1475, 1450, 1325 cm^{-1}; mass spectrum, m/e 363, 365 (parent ions); high resolution mass spectrum for $C_{15}H_{16}NO_3{}^{35}Cl_3$, calcd 363.0196, found 363.0196.

[4(*R*,S),5(*R*,S**)-*cis*]-2-Phenyl-4-benzyl-5-[1(*S*,R**)-hydroxyethyl]-2-oxazoline (13b).** Intramolecular opening of **3b** using the standard Amberlite resin procedure described for **3a** afforded a 1:1 mixture of two isomers. Separation of this mixture by chromatography (silica gel, CH_2Cl_2) provided **13b** in 36% yield along with 33% of the related oxazine. Resubjection of the oxazine to the reaction conditions led to the same 1:1 mixture. Data for **13b**: ^{1}H NMR ($CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 2 H, aromatic), 7.40 (m, 8 H, aromatic), 4.63 (m, 1 H, H_4), 4.52 (dd, J = 3, 9 Hz, 1 H, H_5), 4.13 (m, 1 H), 3.14 (d, J = 7 Hz, 2 H), 1.34 (d, J = 7 Hz, 3 H); when δ 3.14 is irradiated, δ 4.63 collapses to a doublet (J = 9 Hz); IR ($CHCl_3$) 3590, 2980, 1650, 1490, 1450, 1200 cm^{-1}; mass spectrum, m/e 281 (parent ion); high resolution mass spectrum for $C_{18}H_{19}NO_2$, calcd 281.1416, found 281.1419. Data for [4(*R**,*S**),5(*R**,*S**),6(*S**,*R**)]-2-phenyl-4-benzyl-5-hydroxy-6-methyl-5,6-dihydro-1,3-4*H*-oxazine: ^{1}H NMR ($CDCl_3$) δ 7.95 (dd, J = 2,6 Hz, 2 H, aromatic), 7.32 (m, 8 H, aromatic), 4.32 (dq, J = 2, 7, 1 H), 3.85 (m, 1 H), 3.63 (dd, J = 2, 2 H, 1 H), 3.20 (dd, J = 4, 14 Hz, 1 H), 2.64 (dd, J = 9, 14 Hz, 1 H), 1.40 (d, J = 7 Hz, 3 H); IR ($CHCl_3$) 3590, 2930, 1650, 1490, 1450, 1200 cm^{-1}; mass spectrum, m/e 281 (parent ion); high resolution mass spectrum for $C_{18}H_{19}NO_2$, calcd 281.1416, found 281.1416.

[4(*R*,S),5(*S*,R**)-*trans*]-2-Phenyl-4-benzyl-5-[1(*R*,S**)-hydroxyethyl]-2-oxazoline (14b).** This compound was isolated as the minor product of the epoxidations of **1b** specified in Table I; R_f 0.23 (1:1 ether–hexane, 3 developments); ^{1}H NMR ($CDCl_3$) δ 7.95 (dd, J = 1, 8 Hz, 2 H, aromatic), 7.44 (m, 3 H, aromatic), 7.25 (m, 5 H, aromatic), 4.22 (m, 1 H), 4.19 (m, 1 H), 3.56 (dq, J = 6, 6 Hz, 1 H), 3.23 (dd, J = 5, 14 Hz, 1 H), 2.73 (dd, J = 8, 13 Hz, 1 H), 1.23 (br s, 1 H, OH), 0.91 (d, J = 6 Hz, 3 H); IR (CH_2Cl_2) 3600, 2940, 1650, 1500, 1455 cm^{-1}; mass spectrum, m/e 382 (M^+ + H); high resolution mass spectrum for $C_{11}H_{12}NO_2$, calcd 190.0868, found 190.0868.

[4(*R*,S),5(*R*,S**)-*cis*]-2-(Trichloromethyl)-4-benzyl-5-[1(*S*,R**)-acetoxyethyl]-2-oxazoline (15).** Standard intramolecular epoxide opening of 100 mg (0.31 mmol) of **5a** gave 97 mg (97%) of a low melting solid after chromatography (silica gel preparative TLC, 1:1 ether–hexane): ^{1}H NMR ($CDCl_3$) δ 7.24 (m, 5 H, aromatic), 4.54 (m, 2 H), 4.10 (m, 1 H), 3.12 (dd, J = 7, 17 Hz, 1 H), 2.90 (dd, J = 9, 17 Hz, 1 H), 1.53 (d, J = 8 Hz, 1 H, OH), 1.34 (d, J = 8 Hz, 3 H); IR ($CHCl_3$) 3610, 2960, 1660 cm^{-1}; mass spectrum, m/e 321 (parent ion); high resolution mass spectrum for $C_{13}H_{14}NO_2Cl_3$, calcd 321.0090, found 321.0088. This material was acetylated (Ac_2O, DMAP, and pyridine) to give **15** in 95% yield: ^{1}H NMR ($CDCl_3$) δ 7.30 (m, aromatic), 5.20 (dq, J = 6, 6 Hz, 1 H, CHOAc)), 4.94 (dd, J = 6, 10 Hz, 1 H, H_5), 4.70 (m, 1 H, H_4), 2.97 (d, J = 4 Hz, 1 H), 2.96 (d, J = 2 Hz, 1 H), 1.41 (d, J = 6 Hz, 3 H).

6(*E*)-Hepta-1,4-dienyl Trichloroacetamidate (20). Allylic alcohol **19**[8b] (1.0 g, 8.91 mmol) was converted into 2.12 g (93%) of **20** by using the procedure described for preparation of **2a**: ^{1}H NMR ($CDCl_3$) δ 8.25 (br s, 1 H, NH), 5.83 (m, 2 H), 5.59 (m, 1 H), 5.46 (m, 1 H), 5.03 (dd, J = 16, 1 Hz, 1 H, H_{1E}), 5.01 (d, J = 11 Hz, 1 H, H_{1Z}), 2.80 (t, J = 5 Hz, 2 H, H_3), 1.42 (d, J = 6 Hz, 3 H, H_7); IR (neat) 3350, 2990, 1660, 1450, 1290, 1070, 1030, 965, 910, 865, 795, 635 cm^{-1}.

***N*-[(*E*)-Hepta-1,5-dien-4-yl]trichloroacetamide (21).** A solution of **20** (2.10 g, 8.19 mmol) in 25 mL of xylene was heated at reflux for 8 h. The solvent was removed in vacuo and the product purified by chromatography (silica gel, 10:1 hexane–ether), yielding 1.52 g (72%) of **21** as a low-melting solid: ^{1}H NMR ($CDCl_3$) δ 6.58 (br s, 1 H, NH), 5.72 (complex m, 2 H), 5.43 (m, 1 H), 5.14 (dd, J = 11, 2 Hz, 1 H, H_{1Z}), 5.13 (dd, J = 16, 2 Hz, 1 H, H_{1E}), 4.44 (m, 1 H, H_4), 2.38 (m, 2 H, H_3), 1.70 (dd, J = 8, 1 Hz, 3 H, H_7); IR (neat) 3325, 2930, 1710, 1690, 1500, 1440, 1250, 967, 920, 825, 745, 680 cm^{-1}; mass spectrum, m/e 220 (M^+ – Cl). Anal. Calcd for $C_9H_{12}NOCl_3$: C, 42.13; H, 4.71; N, 5.46. Found: C, 42.40; H, 4.72; N, 5.24.

***N*-(*xylo*-5,6-Epoxyhept-1-en-4-yl)trichloroacetamide (22) and *N*-(*lyxo*-5,6-Epoxyhept-1-en-4-yl)trichloroacetamide (23).** A solution of **21** (0.511 g, 1.99 mmol) in 15 mL of dry CH_2Cl_2 was treated with MCPBA (0.456 g, 76%, 2.01 mmol) at 23 °C for 63 h by using the general procedure described previously. The crude product was purified by chromatography (silica gel, 1:1 ether–hexane) to give 91 mg (18%) of recovered **21**, 182 mg (36%; 42% based on consumed **21**) of xylo epoxide **22**, 63 mg (12%; 14% based on consumed **21**) of lyxo isomer **23**, and 61 mg (11%) of a diastereomeric mixture of diepoxides.

Data for **22**: R_f 0.56 (1:1 ether–hexane); ^{1}NMR ($CDCl_3$) δ 6.65 (br, s, 1 H, NH), 5.79 (m, 1 H, H_2), 5.16 (d, J = 16 Hz, 1 H, H_{1E}), 5.15 (d, J = 11 Hz, 1 H, H_{1Z}), 4.27 (dt, J = 7, 7 Hz, 1 H, H_4), 2.84 (m, 2 H, H_5, H_6), 2.46 (t, J = 6.5 Hz, 2 H, H_3), 1.31 (d, J = 5 Hz, 1 H, H_7); IR (CH_2Cl_2) 3475, 2990, 1710, 1500, 1385, 1030, 1005, 935, 830 cm^{-1}; mass spectrum, m/e 230, 232, 234, 236 ($M^+ - C_3H_7$). Anal. Calcd for $C_9H_{12}NO_2Cl_3$: C, 39.66; H, 4.44; N, 5.16. Found: C, 39.57; H, 4.41; N, 5.06.

Data for **23**: R_f 0.51 (1:1 ether–hexane); NMR ($CDCl_3$) δ 6.65 (br s, 1 H, NH), 5.79 (m, 1 H, H_2), 5.17 (dd, J = 17, 1 Hz, 1 H, H_{1E}), 5.15 (d, J = 11 Hz, 1 H, H_{1Z}), 3.83 (m, 1 H, H_4), 3.09 (dq, J = 1, 5 Hz, 1 H, H_6), 2.72 (dd, J = 2, 6 Hz, 1 H, H_5), 2.47 (dd, J = 7, 15 Hz, 1 H, H_{3a}), 2.36 (dd, J = 7, 15 Hz, 1 H, H_{3b}), 1.30 (d, J = 5 Hz, 3 H, H_7); IR (CH_2Cl_2) 3400, 2900, 1720, 1500, 850 cm^{-1}; mass spectrum, m/e 230, 232, 234 ($M^+ - C_3H_7$). Anal. Calcd for $C_9H_{12}NO_2Cl_3$: C, 39.66; H, 4.44; N, 5.16. Found: C, 39.89; H, 4.52; N, 5.09.

[*ribo*-4(*R*,S),5(*R*,S**)]-2-(Trichloromethyl)-4-(1-prop-2-enyl)-5-[1(*S*,R**)-hydroxyethyl]-2-oxazoline (24).** Epoxide **22** (82 mg, 0.30 mmol) was treated with Amberlite resin (0.8 mL in MeOH, IRA-400 in CO_3 form) in MeOH at reflux for 4 h by using the general procedure described previously. Filtration and removal of the solvent in vacuo provided 79 mg (96%) of **24** as a viscous liquid that was pure enough for use directly in subsequent reactions: NMR ($CDCl_3$) δ 5.96 (m, 1 H), 5.19 (dd, J = 17, 1 Hz, 1 H), 5.13 (dd, J = 4, 1 Hz, 1 H), 4.60 (dd, J = 7.7, 9.1 Hz, 1 H, H_5), 4.44 (m, 1 H, H_4), 4.14 (m, 1 H), 2.66 (m, 1 H), 2.47 (m, 1 H), 1.69 (br s, 1 H, OH), 1.38 (d, J = 6 Hz, 3 H); irradiation at δ 2.55 caused δ 5.96 to collapse to a dd, J = 10, 17 Hz, and δ 4.44 to collapse to a doublet, J = 8.8 Hz; IR (neat) 3600–3100, 2950, 1660, 1440, 1375, 1330, 1230, 1100, 980, 910, 825, 785 cm^{-1}; mass spectrum, m/e 271 and 273 (parent ions); high resolution mass spectrum for $C_9H_{12}NO_2Cl_3$, calcd 270.9933, found 270.9930.

By using the same procedure, epoxide **23** (25 mg, 0.92 mmol) was converted into 25 mg (100%) of oxazoline **26**: ^{1}H NMR ($CDCl_3$) δ 5.73 (m, 1 H), 5.17 (d, J = 15 Hz, 1 H), 5.16 (d, J = 12 Hz, 1 H), 4.43 (dd, J = 6, 4 Hz, H_5), 4.28 (ddd, J = 6, 6, 6 Hz, 1 H, H_4), 4.00 (m, 1 H), 2.52 (dd, J = 6, 13 Hz, 1 H), 2.41 (dd, J = 6, 13 Hz, 1 H), 1.77 (br s, 1 H, OH), 1.19 (d, J = 6.6 Hz, 3 H); irradiation at δ 2.46 caused δ 5.73 to collapse to a doublet of doublets, J = 10, 17 Hz, and δ 4.28 to collapse to a doublet, J = 6 Hz; IR ($CHCl_3$) 3610, 3005, 1660, 1430, 1375, 1200, 1000, 920, 835 cm^{-1}; mass spectrum, m/e 271, 273 (parent ions); high resolution mass spectrum for $C_9H_{12}NO_2Cl_3$, calcd 270.9933, found 270.9934.

A sample of oxazoline **24** (18.5 mg, 0.068 mmol) was acylated with acetic anhydride in pyridine to give 19.5 mg (91%) of monocoacetate. This experiment establishes that **24** is in fact an oxazoline and not the six-membered oxazine: NMR ($CDCl_3$) δ 5.91 (m, 1 H), 5.15 (m, 3 H), 4.87 (dd, J = 5.6, 9.5 Hz, 1 H, H_5), 4.53 (dt, J = 9.5 Hz, 1 H, H_4), 2.42 (t, J = 7 Hz, 2 H), 1.35 (d, J = 6.2 Hz, 3 H); irradiation at δ 2.42, caused δ 4.53 to collapse to a doublet, J = 9.5 Hz, and δ 5.91 to collapse to a doublet J = 10, 17 Hz; IR (neat) 2990, 1735, 1660, 1440, 1372, 1335 cm^{-1}; mass spectrum, m/e 316, 314 (parent ion +H).

Similarly, acetylation of **26** provided the corresponding oxazoline monoacetate: NMR ($CDCl_3$) δ 5.70 (m, 1 H), 5.18 (m, 2 H), 5.09 (dq, J = 3, 6.6 Hz, 1 H), 4.54 (dd, J = 3, 6 Hz, 1 H, H_5),

4.23 (dt, J = 6, 6 Hz, 1 H, H_4), 2.47 (complex multiplet, 2 H), 1.20 (d, J = 6.6 Hz, 3 H).

***N*-(*ribo*-5,6-Dihydroxyhept-1-en-4-yl)benzamide (25).** A mixture of oxazoline **24** (90.8 mg, 0.33 mmol) in 6 mL of aqueous HCl (3 M) and 6 mL of MeOH was heated at reflux for 8 h. The solvents were then removed in vacuo to give 85 mg of crude amine salt: ^{1}H NMR (D_2O) δ 5.56 (m, 1 H, H_2), 5.10 (d, J = 18 Hz, 1 H, H_{1E}), 5.11 (d, J = 9 Hz, 1 H, H_{1Z}), 3.61 (m, 1 H), 3.45 (complex m, 2 H), 2.45 (m, 1 H), 2.16 (m, 1 H), 1.11 (d, J = 6 Hz, 3 H, H_7); IR (film on CaF_2 plate) 3600–3050, 2970–2800, 1575, 1485 cm^{-1}.

The crude product obtained above (85 mg) was dissolved in 2.1 mL of acetone and treated with 5.2 mL of saturated aqueous $NaHCO_3$. Benzoyl chloride (0.12 mL, 1.02 mmol) was then added and the mixture stirred for 45 min at 23 °C. The acetone was then evaporated in vacuo, 10 mL of saturated aqueous NaCl was added, and the resulting mixture was extracted with EtOAc (4 × 25 mL). The organic layer was dried, filtered, and concentrated in vacuo to give crude **25**. Purification of this material by chromatography on a 0.5-mm preparative TLC plate with ether gave 54 mg (65% for two steps) of pure **25**: mp 137–138 °C; R_f 0.25 (ether); ^{1}H NMR ($CDCl_3$) δ 7.73 (d, J = 7 Hz, 2 H), 7.45 (m, 3 H), 6.32 (d, 8 Hz, NH), 5.86 (m, 1 H, H_2), 5.15 (dd, J = 1, 17 Hz, H_{1E}), 5.12 (d, J = 10 Hz, H_{1Z}), 4.27 (m, 1 H), 3.80 (m, 1 H), 3.60 (m, 1 H), 3.30 (d, J = 6 Hz, 1 H, OH), 2.57 (m, 2 H, H_3), 1.94 (d, J = 6 Hz, 1 H, OH), 1.31 (d, J = 6 Hz, 3 H, H_7); IR (KBr pellet) 3600–3100, 3080, 2980, 1610, 1540, 1435, 1335, 1310, 1060, 910, 690 cm^{-1}; mass spectrum, m/e 250 (parent ion + H). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.38; H, 7.97; N, 5.64.

Amide **25** was also prepared by reduction of diol azide i[8b,24] (9.7 mg, 0.057 mmol) with triphenylphosphine (15.4 mg, 0.059 mmol) in THF for 42 h. Water (10 μL, 0.55 mmol) was added, and the solution was stirred at 23 °C for 21 h. The THF was removed in vacuo, and 0.37 mL of acetone, 0.84 mL of saturated aqueous $NaHCO_3$, and benzoyl chloride (21 μL, 0.18 mmol) were added. This mixture was stirred for 70 min at 23 °C and then was worked up as described above. In this manner 6 mg (43%) of **25** was obtained following silica gel chromatography.

(±)-*N*-Benzoylristosamine (16). A solution of **25** (27 mg, 0.108 mmol) in 2 mL of MeOH at −20 °C was treated with a stream of O_3 in O_2. Excess O_3 was removed by purging the system with N_2 and then 2 mL of SMe_2 was added. This mixture was stirred for 20 h at 23 °C. All volatile components were removed in vacuo, and the crude product was purified by chromatography (silica gel, ether) to give 21.4 mg (76%) of **16** as a white solid (mp 137–138 °C, recrystallized from EtOAc). This material proved to be a mixture of pyranose and furanose anomers by NMR analysis. The ^{13}C data were in excellent agreement with literature values:[26] ^{13}C NMR (DMSO) δ 166.0, 165.8, 134.2, 131.3, 131.2, 131.1, 130.9, 128.8, 128.2, 128.1, 128.0, 127.7, 127.5, 127.2, 127.1, 126.7, 97.1, 96.9, 90.0, 87.0, 85.7, 71.2, 71.0, 69.5, 67.6, 66.8, 65.1, 49.7, 48.5, 33.9, 19.1, 18.9; IR ($CHCl_3$) cm^{-1} 3600, 3420, 3000, 1640, 1520, 1050; mass spectrum, m/e 251 (parent ion); high resolution mass spectrum for $C_{13}H_{17}NO_4$, calcd 251.1157, found: 251.1156.

Methyl (*Z*)-3-(*N*-Trichloroacetamido)-4-hexanoate (30). A solution of azetidinone **29** (1.36 g, 12.3 mmol) in 20 mL of MeOH was added to a solution of HCl in 190 mL of MeOH (a stream of HCl gas was bubbled into MeOH for 30 min) at 0 °C. The reaction was stirred at 23 °C for 1 h and then was heated to 60–70 °C for 3.5 h. The solvent was removed in vacuo to give 2.06 g (94%) of a yellow solid (mp 125–128 °C, recrystallized from CH_2Cl_2/hexane): ^{1}H NMR (D_2O) δ 5.84 (dq, J = 11, 7 Hz, 1 H, H_5), 5.32 (ddd, J = 11, 11, 1 Hz, H_4), 4.50 (ddd, J = 7, 7, 10 Hz, H_3), 2.80 (dd, J = 17, 7 Hz, 1 H, H_{2a}), 2.69 (dd, J = 17, 7 Hz, 1 H, H_{2b}), 1.63 (dd, J = 7, 2 Hz, 3 H, H_6); IR ($CHCl_3$) 3300–2650 (very broad), 2975, 1730 cm^{-1}.

Trichloroacetyl chloride (0.251 mL, 2.24 mmol) was added to a solution of the amino ester hydrochloride prepared as described above (284 mg, 1.59 mmol) in 2.5 mL of dry pyridine. The reaction was stirred at 23 °C for 5 h. MeOH (3 mL) was then added and the solution stirred for 10 min. The solvent was removed in vacuo, and the resulting crude product was purified by chromatography (silica gel, CH_2Cl_2) to afford 329 mg (72%) of **30** as very pale yellow, low melting solid: ^{1}H NMR ($CDCl_3$) δ 7.64 (br s, 1 H, NH), 5.68 (dq, J = 10, 7 Hz, 1 H, H_5), 5.44 (ddd, J = 9, 9, 1 Hz, 1 H, H_4), 5.00 (m, 1 H, H_3), 2.72 (dd, J = 5, 16 Hz, 1 H, H_2), 2.69 (dd, J = 5, 16 Hz, 1 H, H_2), 1.73 (dd, J = 7, 1 Hz, 3 H, H_6); IR ($CHCl_3$) 3440, 2975, 1735, 1750, 1745, 1500, 1430, 1355 cm^{-1}; mass spectrum, m/e 252, 254 (parent ions − Cl). Anal. Calcd for $C_9H_{12}NO_3Cl_3$: C, 37.46, H, 4.19, N, 4.85. Found: C, 37.63; H, 4.17; N, 5.05.

Epoxidation of 30. Standard MCPBA epoxidation (CH_2Cl_2, 0 °C) performed on 56 mg (0.194 mmol) of **30** provided a 56:44 mixture of **31**:**32**. Separation of the diastereomers was accomplished by preparative TLC (1:1 ether/hexane), giving 29 mg (49%) of **31** and 22 mg (37%) of the arabino isomer **32**.

When the epoxidation of **30** (54 mg, 0.19 mmol) was performed by using the standard $Mo(CO)_6$/TBHP procedure in refluxing benzene a 46:54 mixture of **31**:**32** was obtained (NMR analysis). Separation of the crude product by chromatography as described above gave 9 mg of recovered **30**, 20 mg (35%) of **31**, and 24 mg (41%) of **32**.

Data for **31**: mp 84–86 °C; R_f 0.10 (1:1 ether/hexane); NMR ($CDCl_3$) δ 7.12 (d, J = 7 Hz, 1 H, NH), 3.95 (m, 1 H, H_3), 3.74 (s, 3 H, OCH_3), 3.18 (dq, J = 5, 5 Hz, 1 H, H_5), 3.10 (dd, J = 4, 8 Hz, 1 H, H_4), 2.88 (dd, J = 4, 17 Hz, 1 H, H_{2a}), 2.77 (dd, J = 6, 17 Hz, 1 H, H_{2b}), 1.40 (d, J = 5 Hz, 3 H, H_6); IR ($CHCl_3$) 3390, 2830, 1720, 1500, 1435, 1365 cm^{-1}; mass spectrum, m/e 288 (M^+ − CH_3). Anal. Calcd for $C_9H_{12}NO_4Cl_3$: C, 35.49; H, 3.97; N, 4.60. Found: C, 35.59; H, 3.97; N, 4.61.

Data for **32**: mp 108–110 °C; R_f 0.15 (1:1 ether–hexane); ^{1}H NMR ($CDCl_3$) δ 7.56 (d, J = 6 Hz, 1 H, NH), 4.09 (m, 1 H, H_3), 3.73 (s, 3 H, OCH_3), 3.20 (complex m, 2 H, H_4, H_5), 2.79 (d, J = 5 Hz, 2 H, H_2), 1.37 (d, J = 5 Hz, 3 H, H_6); IR ($CHCl_3$) 3440, 2960, 1725, 1500, 1430, 1365 cm^{-1}; mass spectrum, m/e 271 (M^+ − CH_4O).

Oxazoline Lactone 33. Standard intramolecular epoxide opening performed on 152 mg (0.499 mmol) of **32** yielded, after chromatography (silica gel preparative TLC, ether), 34 mg (22%) of recovered **32** and 49 mg of **33** (36% (46% based on recovered starting material)): mp 178–181 °C; R_f 0.65 (ether); ^{1}H NMR ($CDCl_3$) δ 5.06 (dd, J = 10, 1 Hz, H_5), 4.92 (ddd, J = 2, 6, 10 Hz, 1 H, H_4), 4.47 (d quart, J = 1, 6.5 Hz, 1 H), 3.07 (dd, J = 2, 16 Hz, 1 H), 2.70 (dd, J = 6, 16 Hz, 1 H), 1.54 (d, J = 6.5 Hz, 3 H); irradiation at δ 4.47 caused δ 5.06 to collapse to a doublet, J = 10 Hz, and δ 1.57 to collapse to a singlet; irradiation at δ 2.70 caused δ 3.07 to collapse to a singlet and δ 4.92 to collapse to a doublet, J = 10 Hz; IR ($CHCl_3$) 2940, 1765, 1600, 1345, 1260, 1125, 1030, 970 cm^{-1}; mass spectrum, m/e 271, 273 (parent ions); high resolution mass spectrum for $C_8H_8NO_3Cl_3$, calcd 270.9570, found 270.9570.

***lyxo*-3-(Benzoylamino)-2,3,6-trideoxyhexano-γ-lactone (34).** Oxazoline lactone **33** (43.6 mg, 0.16 mmol) was hydrolyzed with aqueous HCl in MeOH using the procedure described for hydrolysis of **24**, giving 36 mg of crude *lyxo*-3-amino-2,3,6-trideoxyhexano-γ-lactone hydrochloride: ^{1}H NMR (CD_3OD) δ 4.43 (s, 1 H, H_4), 4.09 (br d, J = 8.9 Hz, 1 H, H_3), 3.97 (br q, J = 6.1 Hz, 1 H, H_5), 3.13 (dd, J = 8.9, 18.9 Hz, 1 H, H_{2a}), 2.53 (d, J = 8.8 Hz, 1 H, H_{2b}), 1.27 (d, J = 6.3 Hz, 3 H, H_6); IR (CH_3CN) 3530–3250, 1790 cm^{-1}.

The crude hydrochloride (theoretically 0.16 mmol) was acylated with benzoyl chloride (50 μL, 0.43 mmol) under the conditions described for preparation of **25** to give 29 mg (73%) of **34** following chromatography (silica gel preparative TLC, ether): mp 137–139 °C; R_f 0.31 (ether); ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 6 Hz, 2 H), 7.43 (m, 2 H), 6.69 (d, J = 6 Hz, 1 H, NH), 4.79 (m, 1 H, H_3), 4.36 (dd, J = 3, 3 Hz, 1 H, H_4), 4.16 (d, q, J = 2.6, 6.5 Hz, 1 H, H_5), 3.16 (dd, J = 9, 18.2 Hz, 1 H, H_{2a}), 2.58 (dd, J = 4.3, 18.3 Hz, 1 H, H_{2b}), 1.33 (d, J = 6.4 Hz, 3 H, H_6); IR ($CHCl_3$) 3540, 3400–3200, 2890, 1770, 1660, 920 cm^{-1}; mass spectrum, m/e 231 (M^+ − H_2O); high resolution mass spectrum for $C_{13}H_{13}NO_3$ (M^+ − H_2O), calcd 231.0895, found 231.0895.

Oxazoline 35. Epoxide **31** (176 mg, 0.578 mmol) was subjected to the standard Amerlite resin treatment, yielding 173 mg (98%) of **35** as a white low melting solid after chromatography (silica gel preparative TLC, ether): ^{1}H NMR ($CDCl_3$) δ 4.53 (m, 2 H, H_3, H_4), 3.99 (br m, 1 H, H_5), 3.72 (s, 3 H, OCH_3), 2.92 (dd, J = 4, 17 Hz, 1 H, H_{2a}), 2.61 (dd, J = 9, 17 Hz, 1 H, H_{2b}), 2.01 (br d, J = 4 Hz, 1 H, OH), 1.31 (d, J = 7 Hz, 3 H, H_6); IR ($CHCl_3$) 3500, 2900, 1745, 1675, 1435 cm^{-1}; mass spectrum, m/e 268 (parent ion − Cl); high resolution mass spectrum for $C_9H_{12}NO_4Cl_2$, calcd 268.0143, found 268.0142.

***xylo*-3-(Benzoylamino)-2,3,5-trideoxyhexano-γ-lactone (36a).** A solution of oxazoline ester **35** (106 mg, 0.348 mmol) in

4 mL of MeOH and 4 mL of 3 N aqueous HCl was heated at reflux for 3 days. The solvent was removed in vacuo to give 80.6 mg of a green solid. The ^{1}H NMR spectrum (CD_3OD) indicated the presence of three compounds: the δ- and γ-lactones and the uncyclized methyl ester. Selective recrystallization from CH_3CN gave the pure γ-lactone: ^{1}H NMR (CD_3OD) δ 4.57 (d, J = 6, 7 Hz, 1 H, H_4), 4.27 (m, 1 H, H_3), 4.12 (q, J = 6.2 Hz, H_5), 3.06 (dd, J = 18, 8.9 Hz, 1 H, H_{2a}), 2.72 (dd, J = 18, 5.4 Hz, 1 H, H_{2b}), 1.37 (d, J = 6.4, 3 H, H_6); IR (crude mixture; CH_3CN) 3420–3200, 2900, 1790, 1720 cm^{-1}.

The mixture of hydrolysis products prepared as described above (50 mg) was benzoylated with benzoyl chloride (60 μL, 0.51 mmol) by using the procedure described for preparation of **25** to give, after preparative TLC (silica gel, ether), 26 mg (48%) of **36** and 8 mg (13%) of methyl *xylo*-3-(benzoylamino)-2,3,6-trideoxyhexonate (**36b**).

Data for **36a**: mp 161–164 °C; R_f 0.42 (ether); ^{1}H NMR ($CDCl_3$) δ 7.78 (m, 3 H), 7.48 (m, 3 H), 5.19 (m, 1 H, H_3), 4.57 (dd, J = 7.7, 1.3 Hz, 1 H, H_4), 4.12 (q, J = 7.1 Hz, H_5), 2.96 (dd, J = 9, 17.9, 1 H, H_{2a}), 2.71 (dd, J = 6.4, 18 Hz, 1 H, H_{2b}), 1.39 (d, J = 6.6 Hz, 3 H, H_6); IR ($CHCl_3$) 3600, 3500–3200, 2975, 1780, 1655, 1520, 1480, 1265, 910 cm^{-1}; mass spectrum, m/e 249 (parent ion); high resolution mass spectrum for $C_{13}H_{15}NO_4$, calcd 249.1001, found 249.0095.

Data for **36b**: R_f 0.24 (ether); ^{1}H NMR ($CDCl_3$) δ 7.78 (m, 2 H), 7.46 (m, 3 H), 7.04 (br d, J = 10 Hz, NH), 4.52 (m, 1 H, H_3), 4.05 (dd, J = 3, 5.6 Hz, 1 H, H_4), 3.71 (q, J = 6 Hz, H_5), 3.69 (s, 3 H, OCH_3), 2.80 (dd, J = 2, 7 Hz, 1 H, H_{2a}), 2.63 (d, J = 7 Hz, 1 H, H_{2b}), 1.74 (br s, 1 H, OH), 1.27 (d, J = 6 Hz, 3 H, H_6); IR ($CHCl_3$) 3600, 3450, 2980, 1760, 1730, 1650, 1585, 1565, 1500, 1475, 1260 cm^{-1}; mass spectrum, m/e 282 (M^+ + H); high resolution mass spectrum for $C_{14}H_{20}NO_5$, calcd 282.1341, found 282.1341.

Epoxidation of Azetidinone 29. The standard MCPBA epoxidation procedure was used with a change in the purification procedure. The *m*-chlorobenzoic acid was removed by filtration, and the crude product was then directly chromatographed (silica gel, 1:1 ether–hexane to ether) to give an inseparable 82:18 mixture of **41** and **42** (95% yield; ratio determined by ^{13}C NMR spectroscopy). When the $Mo(CO)_6$/TBHP procedure was employed, a 79:21 mixture of **41** and **42** was obtained in 89% yield. Data for **41** (obtained on mixture): ^{1}H NMR ($CDCl_3$) δ 6.12 (br s, 1 H, NH), 3.49 (m, 1 H, H_3), 3.15 (m, 2 H), 2.97 (dd, J = 4.4, 8.0 Hz, 1 H), 2.82 (ddd, J = 15.3, 2, 3 Hz, 1 H), 1.32 (d, J = 6 Hz, 3 H, H_6); ^{13}C NMR ($CDCl_3$) δ 167.08, 58.57, 52.46, 46.38, 40.79, 13.29. Data for **42**: ^{13}C NMR ($CDCl_3$) δ 167.85, 57.54, 52.75, 45.07, 42.74, 12.88. Data for mixture: IR ($CHCl_3$) 3425, 3005, 1770, 1340, 1200, 870 cm^{-1}. Anal. Calcd for $C_6H_9O_2N$: C, 56.69; H, 7.14; N, 11.02. Found: C, 56.40; H, 7.17; N, 10.81.

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Registry No. **1a**, 110079-69-1; **1b**, 110079-70-4; **1c**, 110079-71-5; **1d**, 110079-72-6; **2a**, 110096-40-7; **2b**, 110079-73-7; **2c**, 110079-74-8; **3a**, 110079-75-9; **3b**, 110079-77-1; **3c**, 110079-78-2; **3d**, 110079-79-3; **4a**, 110169-88-5; **4c**, 110169-89-6; **5a**, 110169-90-9; **5b**, 110169-91-0; **5c**, 110169-93-2; **6a**, 110169-94-3; **6b**, 110169-92-1; **6c**, 110170-06-4; **7**, 110079-66-8; **8**, 110079-68-0; **10**, 110079-63-5; **11**, 110079-65-7; **12**, 110079-67-9; **13b**, 110079-76-0; **14a** (acetate), 110079-80-6; **14b**, 110169-95-4; **15**, 110169-96-5; **16f** (α-anomer), 110079-88-4; **16f** (β-anomer), 110079-89-5; **16p** (α-anomer), 110170-02-0; **16p** (β-anomer), 110170-03-1; **19**, 89179-22-6; **20**, 110079-83-9; **21**, 110079-84-0; **22**, 110079-85-1; **23**, 110169-97-6; **24**, 110079-86-2; **24** (acetate), 110079-87-3; **25**, 110170-00-8; **26**, 110169-98-7; **26** (acetate), 110169-99-8; **29**, 110079-90-8; **30**, 110079-91-9; **31**, 110079-92-0; **32**, 110079-93-1; **33**, 110079-94-2; **34**, 75812-87-2; **35**, 110079-96-4; **36a**, 75812-90-7; **36b**, 110170-04-2; **41**, 110079-97-5; **42**, 110170-05-3; i, 110170-01-9; propyne, 74-99-7; phenylacetaldehyde, 122-78-1; 1-phenyl-2-phthalimidopent-3-yne, 110079-64-6; 1-(triphenylphosphoranylidene)-2-propanone, 1439-36-7; (*E*)-1-phenylpent-2-en-4-one, 42762-51-6; trichloroacetonitrile, 545-06-2; [4(*R**,*S**),5(*R**,*S**),6(*S**,*R**)]-2-phenyl-4-benzyl-5-hydroxy-6-methyl-5,6-dihydro-1,3-4*H*-oxazine, 110079-82-8; *lyxo*-3-amino-2,3,6-trideoxyhexano-γ-lactone hydrochloride, 110079-95-3.

5-Aza-7-deaza-2′-deoxyguanosine: Studies on the Glycosylation of Weakly Nucleophilic Imidazo[1,2-*a*]-*s*-triazinyl Anions

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5-Aza-7-deaza-2′-deoxyguanosine (**1**) has been synthesized by glycosylation of the anions of the imidazo[1,2-*a*]-*s*-triazines **3** or **4b** with 2-deoxydi-*O*-(*p*-toluoyl)-α-D-*erythro*-pentofuranosyl chloride (**7a**). Glycosylation was carried out under liquid–liquid or solid–liquid phase-transfer conditions with Bu_4NHSO_4 or the cryptand TDA-1 as catalyst as well as in the presence of NaH. In contrast to the stereospecific glycosylation occurring at hard nucleophiles, glycosylation was not stereospecific in the case of weakly nucleophilic imidazo[1,2-*a*]-*s*-triazines; α- and β-anomers were formed by applying the three different glycosylation methods. Configurational as well as conformational parameters of the deoxynucleosides **1** and **2** were determined by one- and two-dimensional FT-NMR spectroscopy. Both anomeric 2′-deoxyguanosine isosteres exhibit the anti conformation at the N-glycosylic bond, a predominant C-2′-endo sugar puckering, and a (−sc) conformation around the C-4′–C-5′ bond.

Introduction

Modified 2′-deoxyribonucleosides—in particular those with an altered nitrogen pattern compared to the parent purines—are of wide biological interest.[1] They can be used for site-directed modification of DNA fragments with respect to the study of DNA structure and DNA-protein recognition.

Recently, we have synthesized 7-deaza-2′-deoxyguanosine, which was incorporated into the recognition sequence of the endodeoxyribonuclease Eco R 1, and have studied the interaction of the resulting oligomer with this enzyme.[2] We now report on the synthesis of the 2′-

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