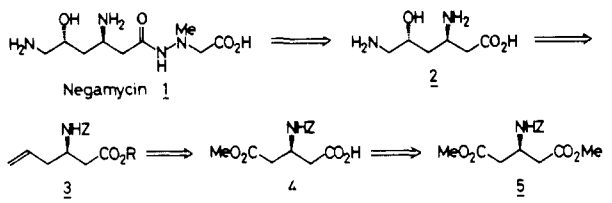
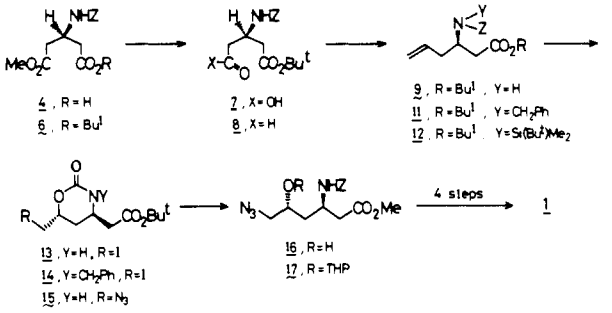
Scheme I



Scheme II



10b/*trans*-**10b**, when *N*-benzyl derivative[6] **9b** was subjected to iodolactonization under the same condition, but this approach (**6** → **9b** → **10b** → **1**) requires more steps for protection and removal of the benzyl group. Next, 1,3-asymmetric induction from the homoallylamino group of **9** was investigated. As illustrated in Scheme II, a new methodology named iodocyclocarbamation has been developed to accomplish the asymmetric functionalization of the double bond. No systematic study on 1,3-asymmetric induction from acyclic homoallylamines has been reported.[7] We found that treatment of **9** with I_2 in CH_2Cl_2 at 0 °C for 24 h resulted in cleavage of the N–Z protecting group to afford the cyclic carbamate **13** in excellent yield,[8] but in this case the desired enantiomer **13**, trans-cyclic carbamate, was obtained as a minor product (3:7 trans/cis). However, we reasoned that if the amino group could be protected further with a more bulky substituent than the CH_2CO_2R group at the α position, the opposite 1,3-asymmetric induction might be realized in a more highly specific manner. Thus, the *N*-benzyl derivative **11**[6,9] was subjected to iodocyclocarbamation (I_2 (3 equiv) in $CHCl_3$, 0 °C, 2.5 h), affording the corresponding cyclic carbamate **14** in 83% yield. The ratio of trans to cis isomers was found to be 23:1 after chromatography on silica gel, showing that a remarkably high 1,3-asymmetric induction was achieved (trans isomer, R_f 0.4; cis isomer, R_f 0.47, AcOEt–C_6H_6 (1:5)). Encouraged by this finding, the *tert*-butyldimethylsilyl (TBDMS) group was selected as a more convenient protective group, because of not only the ready introduction and removal but also the more straightforward synthesis of **1**. The acyclic carbamate **12**, prepared in situ from **9** and TBDMS triflate[10] in the presence of 2,6-lutidine in anhydrous CH_2Cl_2 at 0 °C for 40 min, was directly treated with I_2 (3 equiv) at 0 °C for 2 h. After usual workup and careful TLC on silica gel (3:1 ether/hexane, the desired trans-enantiomer **13** was obtained in 69% yield (mp 114–115 °C, $[\alpha]^{20}_D$ −51.2° (*c* 1.0, $CHCl_3$)), along with the cis isomer in 5% yield, (mp 112–113 °C, $[\alpha]^{20}_D$ −32.5° (*c* 2.0, $CHCl_3$)). The ratio of trans to cis was about 14:1.[11] The high 1,3-asymmetric induction developed here may be reasonably explained by an evaluation of two possible diastereomeric faces of transition-state conformations. The diastereomeric mixture of iodocyclocarbamate **13** was converted to the azidocyclocarbamate **15** in 98% yield. Hydrolysis of **15** with $Ba(OH)_2$ in aqueous THF followed by protection with Z–Cl/$NaHCO_3$ and esterification with CH_2N_2 afforded a diastereomeric mixture of **16** in 85% overall yields. The desired enantiomer **16** was most easily separated at this stage and purified by column chromatography on silica gel (**16**: mp 70–71 °C, $[\alpha]^{20}_D$ +49.8° (*c* 1.0, $CHCl_3$), R_f 0.30, 2:1 ether/hexane). The total synthesis of **1** was completed in five steps from **16** in 51% overall yield (protection of the hydroxyl group with DHP, saponification with 0.25 N NaOH, condensation with benzyl 1-methylhydrazinoacetate by mixed anhydride method,[1b] and removal of the protective group with H_2/Pd–C in aqueous AcOH). The synthetic material ($[\alpha]^{20}_D$ +2.4° (*c* 1.50, H_2O)) was confirmed to be identical with natural negamycin in all respects.[12]

Acknowledgment. This work was supported in part by a Grant-in-Aid for Special Project Research of the Ministry of Education, Science and Culture of Japan.

(6) This derivative was prepared from **6** as follows: (a) H_2–Pd/C, PhCHO, 81%; (b) Z–Cl–Et_3N, 86%; (c) 0.25 N NaOH, 77%; (d) 3,5-dimethylpyrazole–DCC, 89%; (e) $LiAlH_4$, 80%; (f) $Ph_3P^+CH_3I^-$–KH, 95%; (g) *p*-TsOH, 90%.

(7) (a) Fraser-Reid and his co-workers have made significant synthetic advances toward the amino sugar moiety by using oxyamination through five-membered cyclic urethanes from cyclic compounds, while our work is independently in progress. See: Georges, M.; Mackay, D.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1982**, *104*, 1101 and references cited therein. (b) 1,2-Asymmetric induction through five-membered urethanes from epoxy alcohol was achieved in a highly stereocontrolled manner. See: Minami, N.; Ko, S. S.; Kishi, Y. *Ibid.* **1982**, *104*, 1109. (c) 1,2-Asymmetric induction through a five-membered urethane from an epoxy amine was used in sugar chemistry to effect oxyamination. See: Noorzad, H. M.; Gross, D. H. *Carbohydr. Res.* **1973**, *31*, 229.

(8) Bartlett recently observed the similar result by treatment of the *N*-*tert*-butoxycarbonyl derivative of a homoallylic amine with I_2 in CH_3CN. Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *Tetrahedron Lett.* **1982**, *23*, 619.

(9) This compound was prepared from **6** as in the case[6] of **9b** except for the step of hydrolysis with *p*-TsOH.

(10) Corey, E. J.; Cho, H.; Rücker, C.; Hau, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

(11) The silyl derivative **12** was found to be very unstable to result in facile cleavage of the N–Si bond by contact with H_2O. Therefore, it seemed likely that a partial cleavage of the silyl group occurred during the reaction, lowering the overall asymmetric induction.

(12) All new compounds were well characterized by spectroscopic analysis (IR, ^1H NMR, and MS).

1,1-Di-*tert*-butyldiazene

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Contribution No. 6664 from the Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, California 91125

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1,1-Diazenes (aminonitrenes, *N*-nitrenes) are unstable species usually not isolated or directly observed.[2,3] The recent syntheses of kinetically persistent 1,1-diazenes, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene and *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene, have allowed *direct* studies on this species.[4] These five- and six-membered cyclic 1,1-diazenes are equipped with a steric blockade to dimerization and are sufficiently long lived in solution at −78 °C to permit spectroscopic inspection and purification by

(1) Camille and Henry Dreyfus Teacher–Scholar, 1978–1983.

(2) For reviews of 1,1-diazene behavior see: (a) Lemal, D. M. In "Nitrenes"; Lwowski, W., Ed.; Interscience: New York, 1970; Chapter 10. (b) Ioffe, B. V.; Kuznetsov, M. H. *Russ. Chem. Rev.* (*Engl. Transl.*) **1972**, *41*, 131.

(3) For theoretical work on 1,1-diazenes see: (a) Baird, N. C.; Barr, R. F. *Can. J. Chem.* **1973**, *51*, 3303. (b) Lanthon, W. A.; Curtis, L. A.; Helve, W. J.; Lisle, J. B.; Pople, J. A. *Prof. Phys. Org. Chem.* **1974**, *11*, 1975. (c) Ahlrichs, R.; Staemmler, V. *Chem. Phys. Lett.* **1976**, *37*, 77. (d) Wagniere, G. *Theor. Chim. Acta* **1973**, *31*, 269. (e) Baird, N. C.; Wernette, D. A. *Can. J. Chem.* **1977**, *55*, 330. (f) Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 7111. (g) Gelbart, W. M.; Elert, M. L.; Heller, D. F. *Chem. Rev.* **1980**, *80*, 403.

(4) (a) Hinsberg, W. D., III; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608; (b) **1979**, *101*, 6142. (c) Schultz, P. G.; Dervan, P. B. *Ibid.* **1980**, *102*, 878. (d) Schultz, P. G.; Dervan, P. B. *Ibid.* **1981**, *103*, 1563. (e) Dervan, P. B.; Squillacote, M.; Lahti, P.; Sylwester, A.; Roberts, J. D. *Ibid.* **1981**, *103*, 1120. (f) Hinsberg, W. D., III; Schultz, P. G.; Dervan, P. B. *Ibid.* **1982**, *104*, 766. (g) Schultz, P. G.; Dervan, P. B. *Ibid.*, in press.

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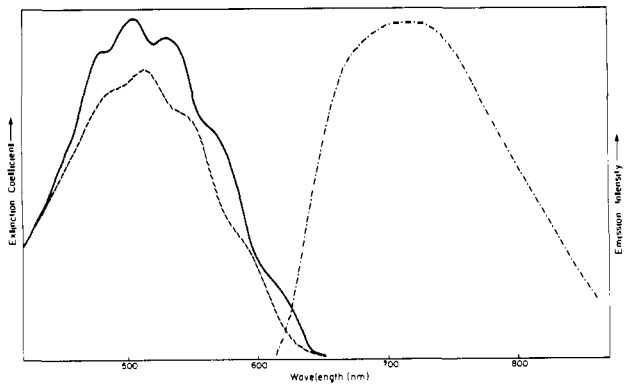
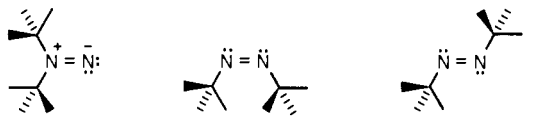


Figure 1. Absorption spectrum of **1** at −127 °C in Me_2O (—) and Me_2O:PrOH (---). Fluorescence spectrum of **1** at −196 °C in Me_2O (-•-).

low-temperature chromatography (−88 °C) for thermal and photochemical studies.[4] Acyclic 1,1-diazenes have so far eluded detection. We report here the synthesis and direct observation of 1,1-di-*tert*-butyldiazene (**1**), an isomer of the characterized azo compounds *cis*- and *trans*-1,2-di-*tert*-butyldiazenes (**2** and **3**).[5]



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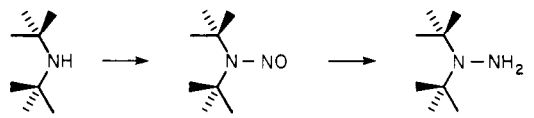
Di-*tert*-butylnitrosamine (**5**) was synthesized from di-*tert*-bu-



4 5 6

tylamine by known procedures.[6] Reduction of di-*tert*-butylnitrosamine (**5**) with sodium in refluxing ethanol under an argon atmosphere afforded the *extremely air-sensitive* 1,1-di-*tert*-butylhydrazine **6**.[7] This was purified by preparative VPC immediately before use.[8] Addition of *tert*-butyl hypochlorite, precooled to −127 °C in CF_3Cl, to a stirred solution of hydrazine **6** and triethylamine in dimethyl ether at −127 °C (*n*-propyl alcohol/liquid nitrogen bath) affords a *red* solution that decolorizes rapidly at −90 °C. Filtration of this colored solution at −127 °C to remove the Et_3NHCl precipitate gives a clear red solution of **1** for spectroscopic analyses.

Low-temperature absorption spectroscopy in the visible region on this solution at −127 °C reveals a structured absorption band with λ_{max} 506 nm (dimethyl ether), presumably the n,π^* electronic transition.[9] Consistent with the n,π^* assignment, use of a more polar solvent, dimethyl ether:propanol (1:1), affords a spectrum shifted 730 cm^{-1} to higher energy.[10] The vibrational spacing in the absorption spectrum is ~1200 cm^{-1}, corresponding to the stretching frequency of the N–N bond in S_1 of **1**. The fluorescence

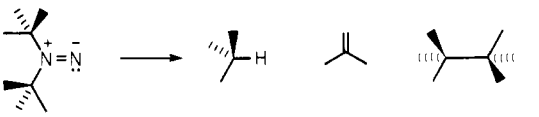
Table I. Relative Rates of Di-*tert*-butyldiazene Decomposition at −94 °C

diazene	solvent	k_{rel}	$\Delta G^{\ddagger}$, kcal mol^{-1}	ref
1	Me_2O	1	12.5	*a*
2	pentane	5×10^{-7}	17.7	*b*
3	hexadecane	2×10^{-34}	40.2	*c*

[a] This work. [b] Reference 15. [c] Reference 16.

spectrum of **1** in dimethyl ether at −196 °C has only a single maximum at 715 nm.[11,12] Warming to −80 °C and recooling to −196 °C result in loss of the fluorescence signal. The λ_{max} of the absorption and emission spectra differ by 209 nm (dimethyl ether), and the spectra differ substantially in shape (Figure 1).[12] These results are not unlike that found for the six-membered cyclic 1,1-diazene *N*-(2,2,6,6-tetramethylpiperidyl)nitrene.[4g]

Low-temperature ^1H NMR spectroscopy (−120 °C, dimethyl ether, 500 MHz) of this red solution reveals a singlet at 1.41 ppm in addition to peaks expected from *tert*-butyl alcohol, triethylamine, and hydrocarbon products **7–9**.[13] The peak at 1.41 ppm, assigned



1 7 8 9

to 1,1-di-*tert*-butyldiazene, disappears simultaneously with the red color when the sample is warmed to −90 °C. The disappearance of this signal at −94 ± 2 °C was monitored with time,[14] and a first-order rate of 1.8×10^{-3} s^{-1} was obtained for decomposition of the 1,1-diazene **1**. Since kinetic parameters for the 1,2-di-*tert*-butyldiazene decompositions are known, relative rates at −94 °C can be calculated for comparison with the 1,1-isomer **1** (Table I). The rate for 1,1-diazene **1** decomposition is 10^6 and 10^{34} times faster than the corresponding *cis*- and *trans*-1,2-diazenes.[15,16] If an Arrhenius preexponential term of 10^{13} is assumed for the unimolecular loss of nitrogen, this rate constant for the decomposition of **1** would place the E_a in the range of 13 kcal/mol.

With regard to product composition, we find that oxidation of 1,1-di-*tert*-butylhydrazine with *tert*-butyl hypochlorite at −78 °C affords hydrocarbons **7–9** in a ratio of 1.0:2.6:0.1. The observed isobutene/isobutane ratio is higher than that observed in the 1,2-diazene thermal decompositions.[17] The extra component of isobutene from the oxidation of hydrazine **6** may arise from some decomposition pathway other than the 1,1-diazene.[18] Consistent with this, the rates of appearance of isobutene and isobutane from the decomposition of **1** followed by low-temperature ^1H NMR appear about equal.[19]

(5) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99 and references cited there.
(6) Back, T. G.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 924.
(7) Hydrazine **6**: IR (film) 3380, 3250, 2990, 1485, 1390, 1370, 1210, 1105, 860 cm^{-1}; NMR ($CDCl_3$) δ 2.9 (s, 2 H), 1.24 (s, 18 H). C, H, N analyses obtained for the benzamide derivative. Anal. Calcd for ($C_{15}H_{24}N_2O$): C, 72.54; H, 9.74; N, 11.28. Found: C, 72.40; H, 9.69; N, 11.11.
(8) Hydrazine **6** was purified by preparative VPC chromatography on a $3 \times {}^1/_4$ in. glass column (Pennwalt 223, 130 °C) and collected under an argon atmosphere.
(9) For example, *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene is red and has λ_{max} (dimethyl ether) = 496 nm.[4f]
(10) See: Huberfield, P.; Lux, M. S.; Rosen, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6828.
(11) The emission spectrum was recorded with the assistance of Professor H. B. Gray's group at Caltech using a noncommercial spectrophotometer with a 200-W mercury–xenon source and Hamamatsu R-406 PMTS. Dimethyl ether:dichloromethane (8:2) formed a glass (−196 °C) for the emission spectra.
(12) Goddard calculated that S_0 of H_2N-N is planar whereas S_1 and T_1 have optimum pyramidal geometries.[3f] One possible explanation for the difference in absorption and fluorescence spectra is vibronic coupling in the pyramidal S_1 state.
(13) We thank William Croasmun for assistance on the 500-MHz NMR. The chemical shift of **1** is relative to acetone internal standard assigned as δ 2.07 at −127 °C.
(14) Methanol chemical shifts were used for temperature calibration.
(15) Schulz, A.; Ruchardt, C. *Tetrahedron Lett.* **1976**, *43*, 3883.
(16) Prochazka, M. *Collect. Czech. Chem. Commun.* **1976**, *41*, 1557.
(17) See: Tanner, D. D.; Rahime, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 255 and references cited there.
(18) In addition to 1,1-diazene **1**, *tert*-butyl chloride and isobutylene are observed in the low-temperature NMR spectra of the products from the reaction of *t*-BuOCl and hydrazine **6**. These products may implicate *tert*-butyl cation as a precursor to some isobutylene. *tert*-Butyl cation could arise from the decomposition of the protonated 1,1-diazene, the di-*tert*-butyldiazenium ion.
(19) Under the reaction conditions the dimer of **1**, 1,1,4,4-tetra-*tert*-butyl-2-tetrazene **10** was not found (<5%) within limits of our detection.[20] The disappearance of 1,1-diazene **1** upon warming, monitored by NMR, is accounted for by the appearance of the three hydrocarbons **7–9**.

Acknowledgment. We are grateful to the National Science Foundation (CHE 80-06495) for support of this research and use of the Southern California NMR Facility supported by NSF Grant CHE 79-16324.

Registry No. 1, 83487-43-8; **4**, 21981-37-3; **5**, 63819-70-5; **6**, 83487-44-9; *tert*-butyl hypochlorite, 507-40-4.

(20) Authentic tetrazene **10** was synthesized by stirring the neat hydrazine **6** under an atmosphere of oxygen at 0 °C. Drying the resulting paste under vacuum afforded white needles: mp 49–50 °C; IR (mull) 2990, 1485, 1395, 1375, 1305, 1200, 1155, 930 cm^{-1}; UV (Et_2O) 230 nm (ϵ 1500); NMR ($CDCl_3$) δ 1.27 (s). Anal. Calcd for $C_{16}H_{36}N_4$: C, 67.55; H, 12.76; N, 19.69. Found: C, 67.29; H, 12.63; N, 19.44.

Synthesis of Saccharides and Related Polyhydroxylated Natural Products. 4. α-D- and β-D-*C*-Glycopyranosides (2,6-Dialkyl-Substituted Tetrahydropyrans)[1]

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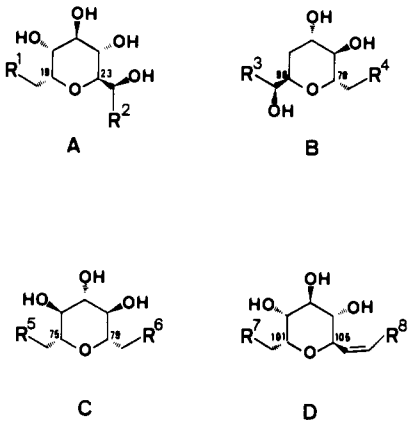
Polyhydroxylated tetrahydropyran rings with two alkyl (or oxygenated alkyl substituents at the 2- and 6-positions[2] of the pyran system represent a basic structural feature of many natural products, which may be regarded as α-D- or β-D-*C*-glycopyranoside derivatives in the context of carbohydrate chemistry. In addition to the synthesis of these natural products, a variety of C-analogues of saccharide phosphates[3] as well as C-linked oligosaccharides are now highly in demand for studies of sugar metabolism. Our attention was initially focused on the *C*-glycopyranosides by an interest in devising a means for stereoselectively constructing the four pyran moieties that constitute fragment A [C(19)–C(23)], B [C(66)–C(70)], C [C(75)–C(79)], and D [C(101)–C(105)] of palytoxin. The fragments are shown with the proposed stereochemistry.[4]



In recent years a variety of synthetic methods for construction of the *C*-glycopyranosides have been developed with *varying* degrees of success.[5] Unfortunately, most, if not all, of these methods did not appear to satisfy our synthetic objective in terms of efficiency, yield, and stereoselectivity, and there was a definite need for further improvement. The new method that we present herein constitutes a general solution for this problem and uses titanium-catalyzed asymmetric epoxidation with diethyl (+)- or (−)-tartrate (DET)[6] to create the crucial C(2) center of the tetrahydropyran system. Our process gives excellent stereoselection and provides the cis- and trans-C(2) and -C(6) substituents with versatile oxygen functionalities for further selective transformation.

Our approach is succinctly demonstrated in Scheme I for the α- and β-D-*C*-glucopyranosides (**1a**, **2a**), as well as their 2-deoxy analogues (**1b**, **2b**). The required starting pyranosides 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (**3a**) and 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-arabinohexopyranose (**3b**) are easily prepared in multigram quantities (five steps in each case)[7] from α-D-glucose pentaacetate and 2-deoxy-D-glucose, respectively. The synthetic process depicted in the scheme proceeds with remarkable facility in both the gluco and 2-deoxygluco series. There are, however, a few aspects worthy of comment. Protection of the free hydroxyl group in **4a** and **4b** was adopted as a conservative measure for these initial studies. All four asymmetric epoxidations (abreviated hereafter as AE) (**5a** → **6a**, **5a** → **7a**, **5b** → **6b**, **5b** → **7b**) proceed in high yield and with excellent (>30:1) diastereoselection under *modified* reaction conditions.[8] The α,β-unsaturated aldehyde corresponding to **5a** and **5b** emerged as a byproduct from AE under standard conditions. The probable culprit in this undesired side reaction is free $Ti(O\text{-}i\text{-}Pr)_4$,[9] and this problem is easily circumvented by increasing the tartrate/$Ti(OiPr)_4$ ratio.[10]

The scheme also reveals that all four intramolecular epoxide openings which provide the desired α- and β-*C*-glycopyranoside diols (**8a**, **8b**, **9a**, **9b**) proceed stereospecifically and in excellent yield. Not surprisingly, these cyclizations occur much more readily in the deoxy series, and both **6b** and **7b** are partially to completely cyclized under the conditions used to remove the silyl protecting group. All four epoxy diols are efficiently cyclized by treatment with sodium hydride in dimethylformamide.

The α- and β-*C*-glycopyranosides (**8a**, **8b**, **9a**, **9b**) are rapidly cleaved by sodium metaperiodate to afford the corresponding (partially or fully) hydrated aldehydes (**1a**, **1b**, **2a**, **2b**), which are cleanly reduced by sodium borohydride to **10a**, **10b**, **11a**, and **11b** in high yield.

The structure of **10a** was unequivocally established by its conversion in two steps (reductive ring opening of the benzylidene

(1) Preceding communication of this series: Lee, A. W. M.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Walker, F. J. *J. am. Chem. Soc.* **1982**, *104*, 3515.

(2) The numbering is based on the tetrahydropyran system.

(3) Nicotra, F.; Ronchetti, F.; Russo, G. *J. Chem. Soc., Chem. Commun.* **1982**, 470 and references quoted therein.

(4) Moore, R. E.; Bartolini, G.; Barchi, J.; Botherner-By, A. A.; Dadok, J.; Ford, J. *J. Am. Chem. Soc.* **1982**, *104*, 3776. Some corrections are made on the proposed stereostructure.

(5) A summary of existing methods for synthesis of *C*-glycopyranosides (and also *C*-glycofuranosides) is given in the supplementary material.

(6) (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, Y.; Ikeda, M.; Sharpless, K. B. *Ibid.* **1981**, *103*, 6237. For the use of the epoxidation for a two-carbon extension, see: (d) Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Tuddenham, D.; Walker, F. J. *J. Org. Chem.* **1982**, *47*, 1373. (e) Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. M. *Ibid.* **1982**, *47*, 1378. (f) Minami, N.; Ko, S. S.; Kishi, Y. *Ibid.* **1982**, *104*, 1109.

(7) Detailed information concerning the synthesis of **3a** and **3b** is provided in the supplementary material.

(8) All reactions were performed at ca. −20 °C in CH_2Cl_2 (0.05–0.1 M in substrate). The "modified" conditions per mole of substrate are as follows: 5 mol of DET, 3.6 mol of $Ti(OiPr)_4$, and 2–4 mol of TBHP. For comparison, the "standard" conditions per mole of substrate are as follows: 1.5 mol of DET, 1.2 mol of $Ti(OiPr)_4$, and 1.5–4 mol of TBHP. We usually start with 2 equiv of TBHP, but when an epoxidation appears to have stopped and unreacted allylic alcohol remains, addition of 1 or 2 further equivalents of TBHP will often drive the reaction to completion. *Regardless of whether "standard" or "modified" AE conditions are employed, we now generally prefer the following new workup procedure* developed by Dr. D. Tuddenham: The reaction mixture (at ca. −20 °C) is diluted with roughly an equal volume of diethyl ether (at room temperature), then saturated sodium sulfate solution (1 mL/mL of $Ti(O\text{-}i\text{-}Pr)_4$ used) is added, and the mixture is stirred vigorously at room temperature for 1–2 h. The heavy precipitate formed is removed by filtration through a Celite pad, and the filtrate is concentrated. Several portions of toluene are added to aid in evaporation of the excess TBHP. Hydrolysis of the tartrate (as in ref 6a except that we now use a saturated brine solution that is 1–2 N in NaOH), or in most cases direct flash chromatography provides the pure epoxy alcohol.

(9) When **5a** was exposed to TBHP and free $Ti(O\text{-}i\text{-}Pr)_4$, it was rapidly and selectively oxidized to the α,β-unsaturated aldehyde.

(10) For a discussion of the effect of the tartrate/$Ti(O\text{-}i\text{-}Pr)_4$ ratio on the presence of "free $Ti(O\text{-}i\text{-}Pr)_4$", see ref 6c.

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