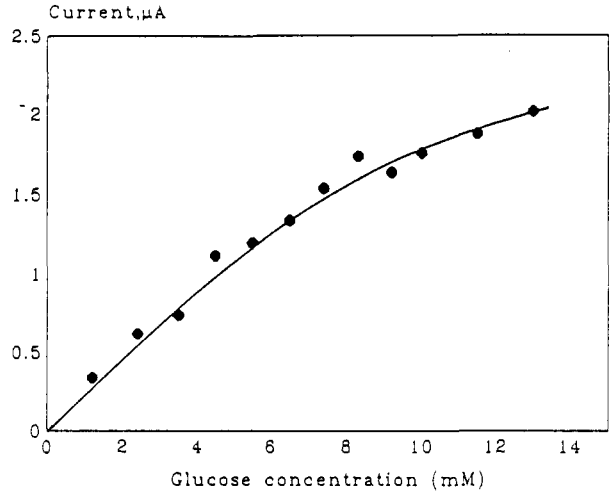


Figure 3. Calibration curve of the glucose biosensor (taken at 700 mV vs SCE).

The following molding procedure was used in order to entrap glucose oxidase in the vanadium oxide matrix. First, 3 g of vanadium pentaoxide (BDH) was fused at 850 °C for 3 h (to increase the V^{4+}/V^{5+} ratio), and it was then quenched in 5 mL of distilled water, forming dark brown vanadium pentaoxide gel. Approximately 1 g of the gel was dissolved in 3 mL of triply distilled water, and the diluted sol was then mixed with 0.25 mL of 6000 units/mL of glucose oxidase solution (EC 1.1.3.4 type VII-S from *Aspergillus niger*, Sigma Chemical Co.), giving a dark brown colloidal suspension. Enzyme electrodes were constructed by dip coating 0.25-mm-diameter Pt wire (Goodfellow, 99.99%) in the vanadium pentaoxide–glucose oxidase solution, followed by overnight drying in ambient conditions.

The immobilization of glucose oxidase in vanadium pentaoxide matrices was carried out by employing a modified protocol of the reported procedures to produce undoped vanadium oxide.[13-15] The enzyme is best added to the colloidal suspension of vanadium oxide before its gelation. Additionally, organic solvents must be excluded from the starting solution due to the insolubility (and denaturation) of enzymes in aprotic solvents. For example, addition of enzyme solution to colloidal suspension of vanadium oxide in acetone–water (as used by Livage et al.[15]) was found to break the suspension and to form voluminous precipitate. Finally, a high-temperature sintering step must be avoided, even at the expense of higher electric resistivity.

Figure 1 is a typical SEM (scanning electron microscopy) photograph of a Pt flag electrode covered by a thin film of vanadium pentaoxide–glucose oxidase in which the porous structure of the vanadium pentaoxide is seen. The same structure (not shown here) is obtained when pure, undoped vanadium pentaoxide xerogel is molded using the same synthetic procedure. The observed porous microstructure is that of bare vanadium pentaoxide surface. Since vanadium pentaoxide is conductive, spattering of the sample with gold was not necessary for SEM studied.

Figure 2 depicts typical room-temperature cyclic voltammetry studies using a PARC EG&G Model 273 potentiostat and three electrode cells, equipped with a Pt-flag counter electrode and saturated calomel electrode (SCE). The applied scan rate was 10 mV/s. The cyclic voltammograms taken at several glucose[16] concentrations show the increase of the current in the potential range of hydrogen peroxide oxidation (ca. 300–600 mV vs SCE). Experiments under nitrogen bubbling did not show any current increase even under high glucose concentrations. This indicates that the biosensing mechanism is via hydrogen peroxide oxidation (generated by enzymatic oxygen reduction) and is not governed by direct charge transfer from the FADH coenzyme to the conductive oxide. Figure 3 demonstrates a typical calibration curve showing the response of the vanadium pentaoxide glucose biosensor (taken at 700 mV vs SCE) to the dissolved glucose level. The metrological characteristics of the vanadium oxide biosensors such as detection range and sensitivity are similar to those of the commercial glucose electrodes.[1] The calibration curve of the vanadium pentaoxide biosensor was stable during prolonged storage, and the electrode did not lose any activity during 10 days of storage at 4 °C. During this period the response of the electrode was checked daily by cyclic voltammetry in blank and in glucose sample solutions.

The sol-gel biosensors, which are exemplified here by the vanadium pentaoxide amperometric prototype, promise to compete well with traditional polymer matrices, currently used in commercial electrochemical biosensors. Although, at this stage, only vanadium pentaoxide-based biosensor is exemplified, the versatility of the sol-gel process promises that other inorganic biosensors will soon emerge, benefiting from the favorable properties of the enormous class of ceramic materials that can be processed by the sol-gel technology.

Acknowledgment. The research is done in collaboration with D. Avnir, M. Ottolenghi, and S. Braun. The research was supported by grants from the Ministry of Science and Technology, Israel, and Forschungszentrum fuer Umwelt and Gesundheit (GSF) GmbH, Neuherberg and the Israel-USA Binational Science Foundation.

(14) (a) Gonzalez-Oliver, C. J. R.; Kato, I. *J. Noncryst. Sol.* **1986**, *82*, 400–407. (b) Dislich, H. *J. Noncryst. Sol.* **1983**, *57*, 371–388. (c) Baddour, R.; Pereira-Ramos, J. P.; Messina, R.; Perichon, J. *J. Electroanal. Chem.* **1991**, *314*, 81–101. (d) Baddour, R.; Pereira-Ramos, J. P.; Messina, R.; Perichon, J. *J. Electroanal. Chem.* **1990**, *277*, 359–366. (e) Lemerle, J.; Nejem, N.; Lefebvre, J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 17–20.

(15) Bullot, J.; Cordier, P.; Gallais, O.; Gauthier, M.; Livage, J. *J. Noncryst. Sol.* **1984**, *68*, 123–134.

(16) Glucose solutions were prepared 24 h before the experiment.

Syntheses and Structure of 8-, 7-, and 6-Membered Silacycloallenes

Yi Pang, Scott A. Petrich, Victor G. Young, Jr., Mark S. Gordon, and Thomas J. Barton*

Ames Laboratory (U.S. Department of Energy) and Department of Chemistry, Iowa State University Ames, Iowa 50011

Received December 11, 1992

Decreasing the ring size of a cyclic allene to rings of fewer than 10 carbons results in deviation of both the normal C=C=C linearity and the orthogonality of the dihedral angle.[1] To date, the smallest isolable cycloallene is 1-*tert*-butyl-1,2-cyclooctadiene,[2] and the smallest for which structural information is available is the phenylurethane derivative of cyclonona-2,3-dien-1-ol,[3] which is bent to 168° and twisted to a dihedral angle of 79.8°. Encouraged by our recent success in the synthesis and structure determination of a tetrasilacyclohexyne,[4] we have pursued the syntheses of strained silacycloallenes and report herein the first examples of isolable 6- and 7-membered rings containing 1,2-diene units.

A key factor in our synthetic success was the finding that 1,3-bis(trimethylsilyl)-1-propyne (**1**) is quantitatively converted to the allenyl dianion **2** upon treatment with 2 equiv of *n*-BuLi in ether.[5] Quenching of **2** with α,ω-dichloropolysilanes **3–5** leads in each case to good yields of the corresponding cyclic allenes **6–8** (Scheme I).

Selected spectral data for **6** (only the second example of an isolable 8-membered cyclic allene), **7**, and **8** (the first examples

(1) For an excellent review of cyclic allenes, see: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(2) Price, J. D.; Johnson, R. P. *J. Org. Chem.* **1991**, *56*, 6372.

(3) Luche, J. L.; Damiano, J. C.; Crabbé, P.; Cohen-Addad, C.; Lajzerowicz, J. *Tetrahedron* **1977**, *33*, 961.

(4) Pang, Y.; Schneider, A.; Barton, T. J.; Gordon, M. S.; Carroll, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 4920.

(5) For a review of propargylic metallation, see: *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed; John Wiley & Sons: New York, 1978; Chapter 9.

0002-7863/93/1515-2534$04.00/0

Table I. Spectral Comparison of Cycloallenes and $(Me_3Si)_4C_3$

allene	GC-IR (cm^{-1})	^{13}C NMR (δ)	^{29}Si NMR (δ)
$(Me_3Si)_4C_3$	1870	203.64, 64.03	−3.93
6	1860	203.41, 62.87	−42.91, −42.13, −16.09, −3.44 (1:2:2:2)
7	1860	204.93, 63.86	−39.28, −16.56, −5.01 (1:1:1)
8	1840	206.11, 63.20	−45.67, −6.88, −6.36 (1:2:2)

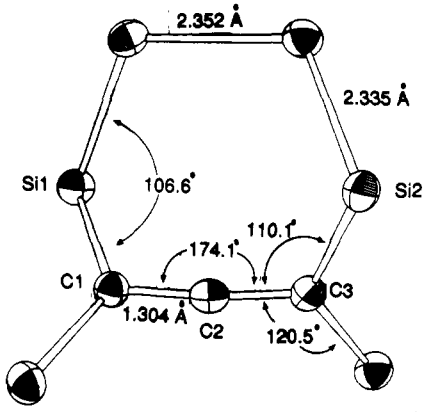
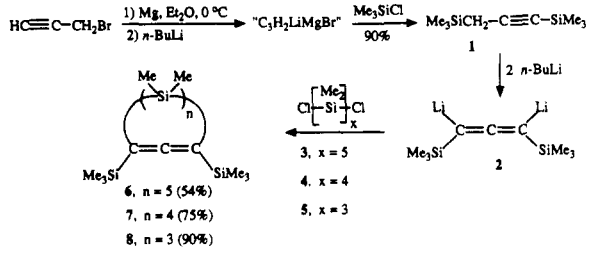


Figure 1. Molecular structure of tetrasilacyclohepta-1,2-diene **7** with selected bond lengths and angles. Methyl groups are omitted for clarity. The molecule is slightly asymmetric in the crystal, so there is not an exact correspondence between bond angles which should be symmetry related.

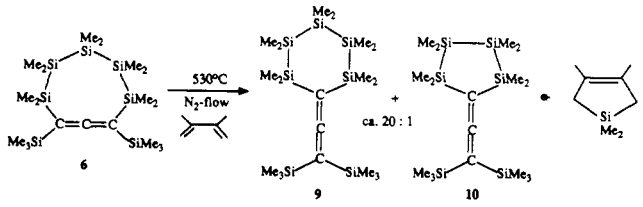
Scheme I



of isolable 7- and 6-membered cyclic allenes) are given in Table I.

As anticipated, allene **6** (mp 230–32 °C) shows no evidence of notable strain; however, the remarkably similar spectral features of **7** and **8** are surprising. In particular, the ^{13}C NMR absorptions and the asymmetric stretch of the allene unit appear relatively insensitive to any changes in carbon hybridization[6] brought about by bending and twisting of the C=C=C unit in these obviously strained rings.

Cyclic allenes **6** and **7** are quite stable and require no special treatment in handling. Cyclohexa-1,2-diene **8** is stable in the absence of oxygen and is extraordinarily unreactive, as evidenced by its inability to react with diphenylbenzisofuran (180 °C for 24 h in decane) or 2,3-dimethylbutadiene (100 °C for 16 h). Gas-phase flow copyrolysis of **6** and excess dimethylbutadiene led predominately (79%) to the isomeric, exocyclic allene **9**[7] and a small amount of ring-contracted allene **10**[8] from Me_2Si: extrusion.



(6) The relationship of bond angles to hybridization will be explored in the full paper along with the problem of defining the dihedral angle for bent and twisted allenes.

(7) **9**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 6 H), 0.15 (s, 12 H), 0.12 (s, 12 H), 0.09 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 202.1, 67.01, 61.91, 0.56, −1.78, −6.47, −6.57; IR (gas phase) 1861 cm^{-1}; mass spectrum m/z 472 (M^+, 36), 457 (14), 399 (57), 229 (23), 73 (100).

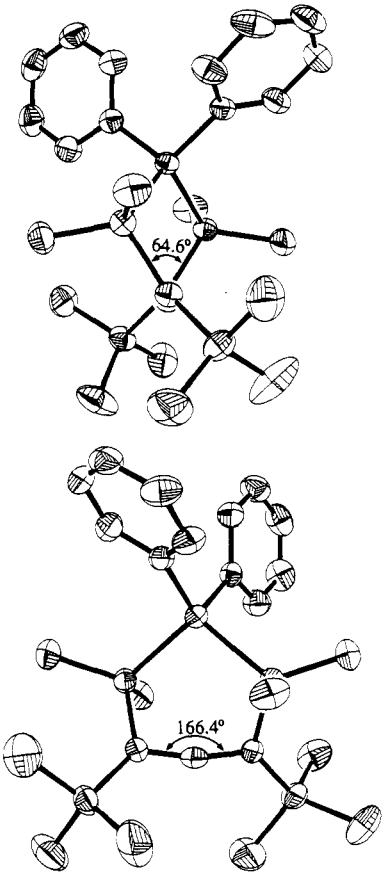
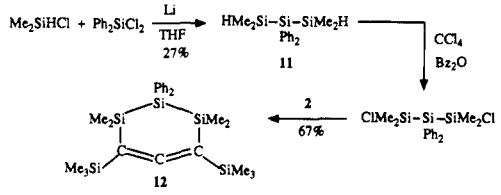
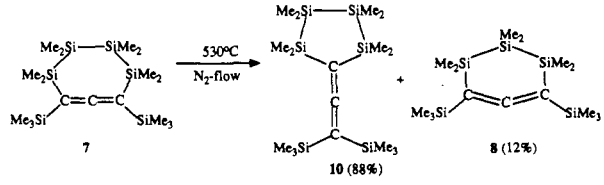


Figure 2. Two ORTEP drawings of **12** to show the bending and twisting of the strained allene unit.

Scheme II



Gas-phase flow pyrolysis of cyclohepta-1,2-diene **7** at 530 °C resulted in 62% conversion with predominant isomerization to exocyclic allene **10** and a small but significant amount of **8**.



Separate pyrolysis of **8** produced no ring-contracted products. Photolysis of **6** produced **7** in 20% yield, but neither **7** nor **8** afforded photoproducts of ring contraction even though Me_2Si: was produced, as evidenced by trapping with Et_3SiH.

(8) **10**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 12 H), 0.15 (s, 12 H), 0.08 (s, 18 H); ^{13}C NMR δ 200.82, 63.58, 63.42, 0.63, −1.99, −7.13; IR (gas phase) 1864 cm^{-1}; mass spectrum m/z 414 (M^+, 35), 399 (14), 341 (77), 73 (100).

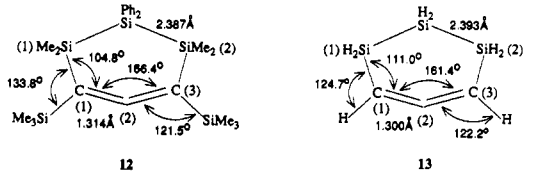


Figure 3. Experimentally (**12**) and theoretically (**13**) determined structures of trisilacyclohexa-1,2-dienes.

The X-ray structure of **7**[9] is shown in Figure 1. Planes defined by the ring silicons and allene carbons (Si(1)C(1)C(2) and Si(2)C(3)C(2)) yield a dihedral angle of 80.1°.[6] The allene unit is bent from linearity to 174.1°.

As cyclohexa-1,2-diene **8** is a liquid, it was necessary to prepare a crystalline derivative (Scheme II). Trisilane **11**[10] was quantitatively dichlorinated in CCl_4, and the resulting 1,3-dichlorosilane was condensed with dianion **2** to afford trisilacyclohexa-1,2-diene **12** in 67% yield as white crystalline needles after purification by GC.

The crystal structure of **12** was solved by direct methods,[11] and the molecular structure is shown in Figure 2. The allene unit is bent to 166.4°, and the dihedral angle, as defined by the Si(1)C(1)C(2) and Si(2)C(3)C(2) planes, is a remarkable 64.6°. Thus, twisting in the trisilacyclohexa-1,2-diene ring is even greater than the previous record of 72.4° measured in octasila[4.4]betweenallene,[12] where only twisting is allowed in fusing an allene simultaneously into two seven-membered rings since the allene must remain linear. Also of interest is the fact that there is considerable rehybridization[6] of the terminal allenic carbons, as evidenced by, for example, the Si(1)C(1)$SiMe_3$ angle of 133.8°, which allows the internal Si—C═C bond angles to reduce to ca. 105° to accommodate a 6-membered ring (Figure 3).

The structure of trisilacyclohexa-1,2-diene **13** was optimized with the 6-31G(d)[13] basis set at the SCF level and verified as a minimum. The calculated and experimental structures (Figure 3) are in reasonable agreement. The dihedral angle is predicted to be 56.2°, significantly smaller than the observed value of 64.6°, and the C═C═C bond angle is calculated to be 161.4°, about 5° less than the experimental value. These two properties are certainly related and are expected to be sensitive to variance in substituents. To assess the possible effect of the ring twisting on the reliability of a single configuration description of the wave function, a TCSCF/6-31G(d) calculation was performed on the ring. The mixing of electron density into the LUMO from the HOMO is essentially 0 (i.e., no diradical character), and thus a single configuration description is valid. The 0 K enthalpy for the MP2[14]/6-31G(d) isodesmic reaction,[15]

$$\mathbf{13} + 2SiH_4 + 2CH_4 \rightarrow 2CH_3SiH_3 + SiH_3SiH_2SiH_3 + H_2C{=}C{=}CH_2$$

is predicted to be 6.3 kcal/mol. This prediction of a stable ring may be compared with our earlier prediction of 18.0 kcal/mol stabilization energy for tetrasilacyclohexyne.[4]

Acknowledgment. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences. Mark S. Gordon acknowledges the support of the National Science Foundation, Grant No. CHE-8911911.

(9) Crystal data for **7** at −50 °C: a = 10.256(1) Å, b = 27.667(6) Å, c = 11.051(4) Å, β = 117.14(2)°, V = 2790(2) Å^3, monoclinic with space group $P2_1/c$, Z = 4, ρ = 0.99 g cm^{-3}. The structure was solved by direct methods, R = 0.037 and R_w = 0.055 for 3817 reflections with $F_o^2 > 2.5\sigma F_o^2$. A complete description is available as supplementary material.

(10) Prepared in 27% yield by lithium-induced coupling of 3 equiv of HMe_2SiCl and 1 equiv of Ph_2SiCl_2. The literature procedure employs HPh_2SiCl and affords a 10% yield of **11**: Gerval, P.; Frainnet, E.; Lain, G.; Moulines, F. *Bull. Soc. Chim. Fr.* **1974**, *7-8*(2), 1548.

(11) **12**: mp 85–87 °C; ^{13}C NMR (less phenyls) δ 207.57 (1 C), 64.14 (2 C), 1.03 (2 C), 0.62 (6 C), 0.06 (2 C); ^{29}Si NMR δ 18.15, −4.69, −5.85; IR (neat film) 1846 cm^{-1}. Crystal data at −60 °C: a = 8.492(2) Å, b = 13.590(3) Å, c = 13.623(3) Å, α = 88.60(2)°, β = 75.94(2)°, γ = 77.53(2), V = 1488.8(4) Å^3, triclinic with space group $P\bar{1}$, Z = 2, ρ = 1.073 g cm^{-3}. The structure was solved by direct methods, R = 0.036 and R_w = 0.053 for 3500 reflections with $F_o^2 > 2.0\sigma F_o^2$. A complete description is available as supplementary material.

(12) Petrich, S. A.; Pang, Y.; Young, V. G., Jr.; Barton, T. J. *J. Am. Chem. Soc.* In press.

(13) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217. Gordon, M. S. *Chem. Phys.* **1980**, *76*, 163.

(14) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1.

(15) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

A New Type of Galactosyltransferase Reaction: Transfer of Galactose to the Anomeric Position of *N*-Acetylkanosamine

Yoshihiro Nishida, Torsten Wiemann, Volker Sinnwell, and Joachim Thiem*

Department of Organic Chemistry
University of Hamburg, Martin-Luther-King Platz 6
D-2000 Hamburg 13, Germany

Received September 2, 1992

Galactosyltransferase from bovine milk (GalT, EC 2.4.1.22) catalyzes the transfer of galactose from UDP-galactose to the OH-4 position of glucose and *N*-acetylglucosamine (GlcNAc). Flexibility of this enzyme allows the transfer of 2-deoxygalactose,[1,2] glucose,[3a] or glucosamine[3b] from corresponding UDP-hexose analogs. Many glucose or GlcNAc derivatives have been tested as acceptors,[4,5] and the structure requirement for the substrate has also been proposed.[6,7] In this communication, we report a quite new type of GalT reaction which involves the regio-mistaken transfer of galactose.

As a part of our synthetic work toward C-3 modified lactose derivatives by chemical and enzymatic means,[8] we have tested GalT reactions with a variety of C-3 modified methyl β-D-glucosides and glucoses in which OH-3 was replaced by H, F, OMe, N_3, or NHAc. The enzymic assay[9] showed that Glc3NAc was the best substrate among them. The relative initial rate at 20 mM was about 3% of the glucose reaction. In order to check the utility of this reaction, Glc3NAc (80 mg, 0.36 mmol)[10,11] and UDP-glucose (205 mg, 0.36 mmol) were reacted in the presence of UDP-glucose epimerase (EC 5.1.3.2, 5 units), GalT (2 units),[12]

(1) Thiem, J.; Wiemann, T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1163.
(2) Thiem, J.; Wiemann, T. *Synthesis* **1992**, 141.
(3) (a) Berliner, L. J.; Robinson, R. D. *Biochemistry* **1982**, *21*, 6340. (b) Palcic, M. M.; Hindsgaul, O. *Glycobiology* **1991**, *1*, 205.
(4) (a) Schanbacher, F. L.; Ebner, K. E. *J. Biol. Chem.* **1970**, *245*, 5057. (b) Morrison, J. F.; Ebner, K. E. *J. Biol. Chem.* **1971**, *246*, 3985. (c) Khatra, B. S.; Herries, D. G.; Brew, K. *Eur. J. Biochem.* **1974**, *44*, 537. (d) Bushway, A. A.; Keena, T. W. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 305. (e) Sinha, S. K.; Brew, K. *Carbohydr. Res.* **1980**, *81*, 239. (f) White, M. D.; Ward, S.; Kuhn, N. J. *Int. J. Biochem.* **1982**, *14*, 449. (g) Palcic, M. M.; Srivastava, O. P.; Hindsgaul, O. *Carbohydr. Res.* **1987**, *159*, 315. (h) Wong, C. H.; Ichikawa, Y.; Krach, T.; Gautheron, C.; Dumas, D.; Look, G. *J. Am. Chem. Soc.* **1991**, *113*, 8137.
(5) (a) Nunez, H. A.; Barker, R. *Biochemistry* **1980**, *19*, 495. For a review, see: (b) Toone, E. J.; Simon, E. S.; Bednarski, M. D.; Whitesides, G. M. *Tetrahedron* **1989**, *45*, 5365. For recent papers, see: (c) Palcic, M. M.; Venot, A. P.; Ratcliffe, R. M.; Hindsgaul, O. *Carbohydr. Res.* **1989**, *190*, 1. (d) Auge, C.; Gautheron, C.; Pora, H. *Carbohydr. Res.* **1989**, *193*, 288. (e) Thiem, J.; Wiemann, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 80.
(6) Berliner, L. J.; Davis, M. E.; Ebner, K. E.; Beyer, T. A.; Bell, E. *Mol. Cell Biochem.* **1984**, *62*, 37.
(7) Wong, C. H.; Lie, K.-K.-C.; Kajihara, T.; Shen, L.; Zhong, Z.; Dumas, D. P.; Liu, J. L. C.; Ichikawa, Y.; Shen, G. J. *Pure Appl. Chem.* **1992**, *64*, 1197.
(8) Partly reported in Nishida, Y.; Thiem, J. XVI International Carbohydrate Symposium, July 5–10, 1992, Paris.
(9) Fitzgerald, D. K.; Colvin, B.; Marval, R.; Ebner, K. E. *Anal. Biochem.* **1970**, *36*, 43.
(10) 3-Acetamido-3-deoxy-D-glucose was prepared by hydrogenation of 3-azido-3-deoxy-D-glucose[11] with $Pd(OH)_2$ followed by N-acetylation with acetic anhydride in methanol and identified by NMR spectroscopy (cf. supplementary material).
(11) Faghih, R.; Escribano, F. C.; Castillon, S.; Garcia, J.; Lukacs, G.; Olesker, A.; Thang, T. T. *J. Org. Chem.* **1986**, *51*, 4558.

0002-7863/93/1515-2536$04.00/0