responsible for epoxidation, or alternatively, complexes may be poor catalysts for epoxidation because they are good catalysts for H_2O_2 disproportionation. Experiments to discriminate between these possibilities are planned.

The complex color changes that we observed when hydrogen peroxide was reacted with iron–cyclam complexes have led us to the conclusion that several intermediate species are involved. However, our attempts to characterize potential intermediates spectroscopically have so far been frustrated by a competing reaction of the ligand. During the course of these reactions, the initially purple complex was converted to a green complex which was no longer active as a catalyst for the epoxidation reaction in acetonitrile. This particular spectroscopic change resembles those that occur when ferrous complexes of related ligands undergo oxidative dehydrogenation upon reaction with dioxygen.[25]

Future studies will focus on attempts to stabilize intermediates in this reaction and to characterize their spectroscopic properties and their reactivities. If non-porphyrin iron complexes are indeed capable of epoxidizing olefins without prior O–O bond cleavage, such a mechanism should be considered in the cases of non-heme iron containing monooxygenase enzymes and iron bleomycin as well.

Acknowledgment. We thank Dr. Y. Wu and Professor K. N. Houk for providing us with Figure 1. Financial support from the National Science Foundation is gratefully acknowledged.

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The Temporary Silicon Connection Method in the Control of Regio- and Stereochemistry. Applications to Radical-Mediated Reactions. The Stereospecific Synthesis of *C*-Glycosides

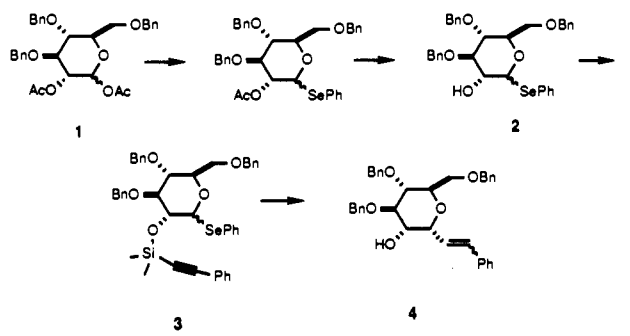
Gilbert Stork,* Hong Suk Suh, and Guncheol Kim

Chemistry Department, Columbia University
New York, New York 10027
Received June 7, 1991

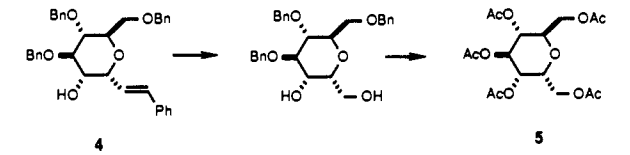
We report in this paper the application of the temporary silicon connection method for the control of regio- and stereochemistry[1] to the synthesis of *C*-glycosides.

C-Glycosides are an important class of carbohydrate derivatives,[2] and numerous methods have been devised for their stereoselective construction.[3] Most of those methods are empirical,

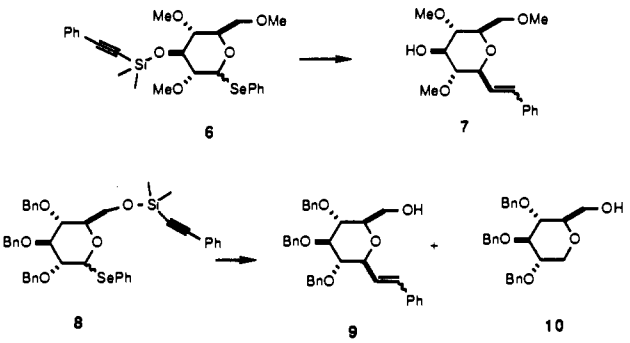
Scheme I



Scheme II



Scheme III



and the result of their use in a previously unstudied case cannot be predicted with confidence.

The method we describe here is entirely general. It achieves the stereospecific introduction of a styryl group at the anomeric center of a particular carbohydrate by the radical-induced[4] cyclization of a 3-phenylethynyl group tethered, via a temporary silicon connection,[5] to a suitable hydroxyl group of the carbohydrate.

In contrast to the poor stereocontrol available via *inter*molecular radical reactions at the anomeric center,[6] the geometric requirements for the *intra*molecular cyclization of an ethynyl group tethered to a β-hydroxyl onto the radical at the anomeric center can only lead, after detachment of the silicon connector, to a β *C*-glycoside (A), while tethering to an α-hydroxyl can only give an α *C*-glycoside (B). This is schematized in Figure 1.

The phenylethynyl group was chosen to be the tethered entity because (1) we have devised a simple method for attaching an acetylene to a hydroxyl via a silicon atom[7] and (2) the presence of a phenyl rather than an alkyl group leads to more general and efficient cyclizations. The styryl *C*-glycosides will sometimes be needed, as such. More generally, the styryl substituents, whatever their geometry, serve as convenient precursors for the stereospecific introduction of a versatile aldehyde or carbinol function at the anomeric center.

(1) The Temporary Silicon Connection has been under investigation at Columbia for several years. Cf.: Keitz, P., ref 5. Stork, G. 32nd National Organic Symposium, Minneapolis, June 1991.

(2) Cf. inter alia: (a) Hanessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111. (b) Nishimura, N.; et al. *J. Antibiot., Ser. A* **1966**, *17*, 148. (c) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309. (d) Connor, D. T.; Greenough, R. C.; v. Strandtmann, M. *J. Org. Chem.* **1977**, *42*, 3664.

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(4) The formation of C-glycosides by *inter*molecular trapping of a radical at the anomeric center of a carbohydrate was first reported by: (a) Giese, B.; Dupuis, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 622. (b) Addlington, R. M.; Baldwin, J. E.; Basak, A.; Kozyrod, R. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1944. For examples of *intra*molecular *C*-glycoside constructions based on radical cyclization, cf.: De Mesmaeker, A.; Hoffmann, P.; Beat, E.; Hug, P.; Winkler, T. *Tetrahedron Lett.* **1989**, *30*, 6311.

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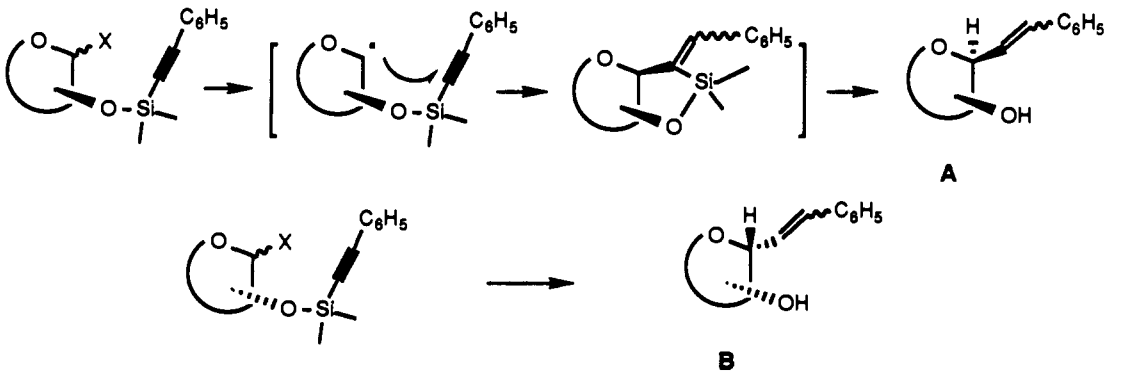


Figure 1.

We now illustrate with specific examples the temporary silicon connection route to either α or β *C*-glycosides in the pyranose (glucose, mannose), as well as in the furanose (ribose, arabinose), series. As shown in Scheme I, the 1,2-diacetate of glucose 3,4,6-tribenzyl ether (**1**)[8] was transformed (PhSeH, BF_3·Et_2O, followed by deacetylation with methoxide–methanol) into the 2-hydroxy phenylselenoglycoside **2**.[9] Reaction with chloro(phenylethynyl)dimethylsilane gave the tethered siloxy intermediate **3**[7] which was then cyclized by refluxing in benzene (0.01 M) with tributylstannane in the presence of AIBN[10] and desilylated, without isolation, by stirring with tetrabutylammonium fluoride in THF[11] to give the desired α *C*-glycoside **4** in 83% overall yield from **3**.

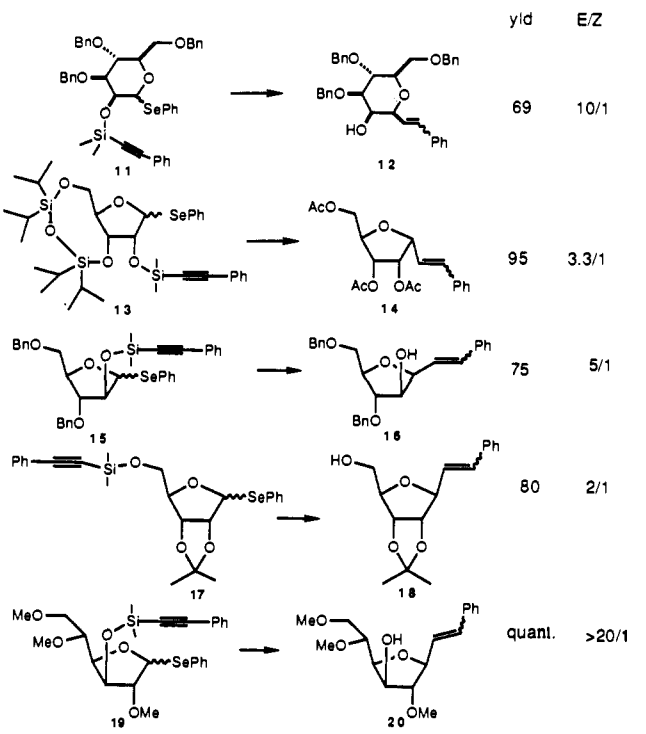
It is of some interest that the 2-phenylethenyl group of **4** was predominantly (10:1) the *E* isomer, a result which appears general[5] in cyclizations of this type.

The structure of the alkenyl *C*-glucoside **4** was readily established. Ozonolysis followed by reduction (O_3, CH_2Cl_2, MeOH; DMS; $NaBH_4$, MeOH) and acetylation gave the known pentaacetate **5**, $[\alpha]_D$ + 48.4 (*c* 0.7 in $CHCl_3$; reported[12] $[\alpha]_D$ + 48.8). The NMR spectrum of the pentaacetate was identical with that of an authentic sample.[12]

The process just described leads, stereospecifically, to α *C*-glucosides. β *C*-glucosides can be obtained by silicon tethering to the 3β-hydroxyl of glucose: this is illustrated, starting with **6**, the phenylethynylsilyl derivative of the phenylselenoglucoside of 2,4,6-tri-*O*-methyl-D-glucopyranose.[13] Cyclization-desilylation, as before, now gave the β *C*-glucoside **7**(*E*/*Z* > 20:1) in 73% yield.[14] This result is especially noteworthy because cyclization involves a conformation in which the 3-siloxy group must become axial.[15]

One might not expect that formation of a β *C*-glycoside by cyclization of a chain tethered to the primary 6-hydroxyl group of glucose, as in **8**,[16] would be an efficient process, involving as it does not only the necessary conformational change to make the hydroxymethyl group axial but also the formation of a 7-membered ring. Nevertheless, the β *C*-glucoside **9** is still obtained in 36% yield (the other product being, not surprisingly, the 1-deoxyglucose derivative **10**). The yield of **9** could be raised to 54% by slow addition of the tin hydride by means of a syringe pump.

Scheme IV



The process described here appears quite general. In the *mannose* series, the tethered phenylacetylene **11**[17] gave the β *C*-mannoside **12**. This is illustrated in Scheme III,[18] which shows that the method is also a very efficient route to *C*-furanosides: the high yield constructions of **14** (after desilylation and acetylation) and of **18** emphasize, for example, how easily *either* α or β *C*-glycosides can be obtained in the ribose series.[18]

One feature of the process deserves a final comment. Transfer of the silicon-connected chain to the anomeric center from a

(8) Ekborg, G.; Lindberg, B.; Lonngren, J. *Acta Chem. Scand.* **1972**, *26*, 3287.

(9) Cf.: Dupuis, J.; Giese, B.; Ruegge, D.; Fischer, H.; Korth, H. G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 896.

(10) This procedure was generally satisfactory for the cyclizations described in this paper. A syringe pump was used in the cyclization of **6** and **11**.

(11) (a) Oda, H.; Sato, M.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron* **1985**, *41*, 3257. (b) Chan, T. H.; Michajlowskij, W. *Tetrahedron Lett.* **1974**, 3479.

(12) Zhai, D.; Zhai, W.; Williams, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 2501. We thank Professor Williams for an authentic sample.

(13) von Freudenberg, K.; Plankehorn, B. *Liebigs Ann. Chem.* **1938**, *536*, 257.

(14) The structure of **7** was easily proved by protection (TBDMS) of the 3-hydroxyl, followed by ozonolysis, reduction, and O-methylation to the 1-β-methoxymethyl derivative, a sequence that led to the expected meso (rotation; ^1H NMR) product.

(15) The success of the reaction may reflect the twist conformation of the anomeric glycosyl radical (cf. ref 9) in which the required axial orientation of the 3-hydroxyl is already achieved.

(16) Made from 2,3,4-tri-*O*-benzylglucopyranose: Eby, R.; Sodheimer, S. J.; Schuerch, C. *Carbohydr. Res.* **1979**, *73*, 273.

(17) From the 2-acetate of 3,4,6-tri-*O*-benzylmannopyranose: Ponpipom, M. M. *Carbohydr. Res.* **1977**, *59*, 311.

(18) It is of interest that we have consistently found the resonance of the hydrogen on the carbon bearing the phenylethenyl group to be at 0.2 to 0.3 ppm lower field in the *Z* than in the *E* isomer.

(19) For the synthesis of the precursors of **13**, **15**, **17**, and **19**, see, respectively: (a) Schaumberg, J. P.; Hokanson, G. C.; French, J. C.; Smal, E.; Baker, D. C. *J. Org. Chem.* **1985**, *50*, 1651. (b) Martin, O. R.; Rao, S. P.; El-Shenawy, H. A.; Kurz, K. G.; Cutler, A. B. *J. Org. Chem.* **1988**, *53*, 3287. (c) Stewart, A. O.; Williams, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 4289. (d) Osman, E. M.; Hobbs, K. C.; Walston, W. E. *J. Am. Chem. Soc.* **1951**, *73*, 2726.

particular hydroxyl group *specifically* releases that hydroxyl, making it available for whatever subsequent transformations might be required. This enlarges considerably the scope of the method: α *C*-mannosides, for example, could, in principle, be made by inversion of the C-2 hydroxyl of the glucose-derived **4** and, similarly, β *C*-glucosides are accessible, not only as shown in **6** to **7**, or **8** to **9**, but also by inversion of the C-2 hydroxyl of **11**.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their support of this work.

High-Driving-Force Electron Transfer in Metalloproteins: Intramolecular Oxidation of Ferrocytochrome *c* by Ru(2,2'-bpy)$_2$(im)(His-33)$^{3+}$

I-Jy Chang, Harry B. Gray,* and Jay R. Winkler*

Contribution No. 8439, Beckman Institute
California Institute of Technology
Pasadena, California 91125

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Electron-transfer (ET) theory describes rates in terms of nuclear-reorganization (λ) and electronic-coupling (H_{AB}) parameters.[1] These parameters are most directly determined from the driving-force dependence of the ET rate (ideally at high driving forces in the neighborhood of λ).[2] Remarkably slow ET rates have been observed at low driving forces ($-\Delta G° < 0.3$ eV) in certain iron–sulfur[3] and blue copper proteins,[4] and at high driving forces in Ru(bpy)$_2$L(His-33) (bpy = 2,2'-bipyridine; L = imidazole, pyridine, H_2O; His = histidine) derivatives of cytochrome *c* (cyt *c*).[5] Since the latter results conflict sharply with the much faster ET rates reported for Ru-modified Zn-substituted cytochrome *c* (Ru-Zn-cyt *c*)[2,6] and Ru(bpy)$_2$(dcbpy)-labeled ferrocytochrome *c* (dcbpy = dicarboxybipyridine),[7,8] we have determined the Ru(bpy)$_2$L(His-33)-cyt *c* kinetics by using a novel flash-quench method that allows the observation of rates over an extremely wide range.[9-11]

The rate of intramolecular oxidation of horse heart ferrocytochrome *c* by Ru(bpy)$_2$(im)(His-33)$^{3+}$ (im = imidazole)[12,13] was measured as outlined in Scheme I. The quencher (Q) used

Scheme I

$$\text{D–A} + h\nu \rightarrow \text{D–A}^* \quad (1a)$$

$$\text{D–A}^* + \text{Q} \rightarrow \text{D–A}^+ + \text{Q}^- \quad (1b)$$

$$\text{D–A}^+ \rightarrow \text{D}^+\text{–A} \quad (1c)$$

$$\text{D}^+\text{–A} + \text{Q}^- \rightarrow \text{D–A} + \text{Q} \quad (1d)$$

in this study was Ru_6^{3+} (a = NH_3). The excited-state decay rates of Ru(bpy)$_2$(im)$_2^{2+*}$ and Ru(bpy)$_2$(im)(His-33)$^{2+*}$-Fe^{II}-cyt *c* do not differ greatly (1.4×10^7 and 1.25×10^7 s^{-1}, respectively), demonstrating a minor role for direct photoinduced ET. The second-order rate constant for oxidative quenching of Ru(bpy)$_2$(im)(His-33)$^{2+*}$-Fe^{II}-cyt *c* by Ru_6^{3+} is 4.9×10^8 M^{-1} s^{-1}. Transient absorption measurements[14] on solutions of Ru(bpy)$_2$(im)(His-33)$^{2+}$-Fe^{II}-cyt *c* (18 μM) and Ru_6^{3+} (7 mM)[15] exhibit biphasic kinetics. The rate constants of both kinetic components are independent of protein concentration. The first process represents decay of Ru(bpy)$_2$(im)(His-33)$^{2+*}$, accelerated by the bimolecular quenching reaction with Ru_6^{3+}. The second process corresponds to the intramolecular oxidation of the ferroheme by Ru(bpy)$_2$(im)(His-33)$^{3+}$ ($k_{ET} = 2.6 \times 10^6$ s^{-1}, T = 298 K, pH = 7, sodium phosphate buffer, μ = 0.1).[16] Identical kinetics were measured at wavelengths characteristic of the heme oxidation state and the Ru oxidation state (306, 400, 500, and 550 nm; Figure 1). This ET rate contrasts with the previously reported rate of 55 s^{-1} measured by pulse radiolysis.[5] The transient absorption spectrum measured upon completion of the second process is identical with the Fe$^{III/II}$-cyt *c* difference spectrum (Figure 2).[17] Over a period of seconds, the photogenerated Ru_6^{2+} reduces the Fe^{III}-cyt *c* formed by intramolecular ET to regenerate the original complex.

Intramolecular ET reactions involving Ru–ammine complexes coordinated to His-33 of Zn-substituted cytochrome *c* (Ru$_4$L(His-33)-Zn-cyt *c*; L = NH_3, pyridine, isonicotinamide) are best described by an electronic coupling matrix element of 0.12 (2) cm^{-1} and a 1.2 (1)-eV reorganization energy.[2] A large part of this reorganization energy involves solvent reorientation around the Ru–ammine complex. It is known, however, that the solvent reorganization energies associated with the ET reactions of Ru–bipyridine complexes are substantially smaller than those of ammine complexes.[18] The self-exchange reorganization energies (λ_{11}) for Ru$_5$(pyridine)$^{3+/2+}$ and Ru(bpy)$_3^{3+/2+}$ are 1.20 and 0.57 eV, respectively.[18] By using the Marcus cross-relation ($\lambda_{12} = {}^1/_2\lambda_{11} + {}^1/_2\lambda_{22}$)[1] and these same reorganization energies for Ru$_4$L(His-33) and Ru(bpy)$_2$(im)(His-33), we estimate λ = 0.89 (10) eV for intramolecular ET in Ru(bpy)$_2$(im)(His-33)-Fe-cyt *c*. The predicted rate of ferroheme oxidation by Ru(bpy)$_2$(im)(His-33)$^{3+}$, 3.5×10^6 s^{-1} (λ = 0.89 eV; H_{AB} = 0.12 cm^{-1}; $-\Delta G°$ = 0.74 eV), is in excellent agreement with that measured by the flash-quench technique. An important advantage of the reduced reorganization energy in Ru(bpy)$_2$(im)(His) (compared to the Ru(a)$_4$L(His)

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(12) Ru(bpy)$_2$(im)(His-33)-Fe-cyt *c* was prepared according to a published procedure[8,13] by the reaction of Ru(bpy)$_2$(CO$_3$) with purified horse heart ferricytochrome *c*, followed by addition of excess imidazole. Details of the preparation, purification, and characterization of this derivatized protein are available as supplementary material.
(13) Durham, B. D.; Pan, L. P.; Hahm, S.; Long, J.; Millett, F. In *ACS Advances in Chemistry Series*; Johnson, M. K., King, R. B., Kurtz, D. M., Kutal, C., Norton, M. L., Scott, R. A., Eds.; American Chemical Society: Washington DC, 1990; Vol. 226, pp 180-193.
(14) Laser: XeCl excimer-pumped dye laser (Coumarin 102); 25-ns pulses at 480 nm; 4 mJ per pulse.
(15) Under these conditions, the equilibrium concentrations of solution species are the following: [Ru(bpy)$_2$(im)(His-33)$^{2+}$-Fe^{II}-cyt *c*] = 18 μM; [Ru(bpy)$_2$(im)(His-33)$^{2+}$-Fe^{III}-cyt *c*] = 5 μM; [Ru_6^{3+}] = 7 mM. Thus, 22% of the ET quenching reactions generate Ru(bpy)$_2$(im)(His-33)$^{3+}$-Fe^{III}-cyt *c*. Independent measurements with the fully oxidized protein exhibit no transient kinetics on the time scale (i.e., $\leq$10 μs) of the intramolecular ET reaction.
(16) We also observe identical ET kinetics for the same reaction when Ru(bpy)$_2$(im)(His-33)$^{3+}$-Fe^{II}-cyt *c* is produced (in low yield) by direct electron transfer from Ru(bpy)$_2$(im)(His-33)$^{2+*}$ to the ferriheme center. This observation provides strong support for our interpretation of the flash-quench kinetics. The photoinduced ET rate does not significantly accelerate the Ru(bpy)$_2$(im)(His-33)$^{2+*}$ decay so that a reliable rate constant for this reaction cannot be extracted from the decay kinetics. Estimates based on the yield of Ru(bpy)$_2$(im)(His-33)$^{3+}$-Fe^{II}-cyt *c* suggest a rate constant of $\sim 2 \times 10^5$ s^{-1}.
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