programs. The E map with the highest parachor value allowed location of the nonhydrogen atoms; all the hydrogen atoms were recognized subsequently via difference electron density syntheses during the refinement. This was performed by isotropic and then anisotropic full-matrix least-squares procedures on carbon and oxygen atoms, with a total number of 181 parameters; the contributions of the hydrogen atoms were included in the structure factor calculations with a thermal factor equal to the U (equivalent) value of the bonded atom. In the final cycle all shifts were less than 0.07σ; the discrepancy index over the 1516 observed reflections converged to $R = 0.051$. A final difference map showed no significant features, the electron density values ranging between +0.22 and −0.24 e $Å^{-3}$.

Theoretical Calculations. Within the framework of second-order perturbation theory and with the assumption that different atoms of the first molecule do not interact at the same time with the same atom of the second one, i.e., considering only two-center interactions, the treatment of Salem and Devaquet[8] leads to three components of the interacton energy (E_{int}) between two conjugated molecules in their ground states. The equations for the closed-shell repulsion term (E_{rep}) and the attractive term (E_{mix}), both of which depend on the overlap between interacting orbitals ($E_{over} = E_{rep} + E_{mix}$), are those reported in ref 8a (eq 15). The equation for the polar term (E_{pol}), representing electrostatic interactions between net charges on the atoms, is eq 31c in ref 8c. For the sake of simplicity, the E_{mix} addend of eq 15 in ref 8a has been simbolyzed as follows: $E_{mix} = [E_\eta(j,k') + E_S(j,k')] + [E_\eta(k,j') + E_S(k,j')]$.

Nonbonded interactions between all pairs of atoms s and s′ of the two addends were treated by using a Lennard–Jones "6-12" potential function.[17] The values of the parameters were the same as those given in Table IV of ref 15.

Resonance integrals $\eta_{rr'}$ were assumed to be proportional to the overlap integral $S_{rr'}$, and the proportionality parameter K was evaluated through the following: (i) the Mulliken approximation[18] where $K = (\beta_r + \beta_{r'})/2$, with $\beta_C = -21$ eV and $\beta_O = -31$ eV; (ii) the Wolfsberg–Helmholtz approximation,[19] where $K = k(H_{rr} + H_{r'r'})$ with $H(2pC) = -11.4$ eV, $H(2pO) = -14.8$ eV, and $k = 1.75/2$. At large distances (5 Å) between the two centers, the variations of η_{CC} and η_{CO} with the distance as calculated by method i are a little more negative than when calculated by method ii, the difference increasing as the distance diminishes. As preliminary calculations have shown that the E_{mix} value is not significantly influenced by the used appoximation, that of Wolfsberg–Helmholz was used.

Overlap integrals were calculated by standard formulas.[20] The deviations of the overlapping orbitals from the alignment required for pure σ overlapping were taken into account by use of the correction $S_{rr'} = S_{rr'}(\sigma,\sigma)\cos^2\theta + S_{rr'}(\pi,\pi)\sin^2\theta$ where the integrals $S_{rr'}(\sigma,\sigma)$ and $S_{rr'}(\pi,\pi)$ were calculated by the standard formulas, and θ is the angle between the line joining atoms r and r′ and the axis of the $2p\pi$ orbitals centered on r and r′ (Figure 4).

The molecular geometries of 2-carbomethoxy-1,4-benzoquinone (**1**) and 1-vinylcyclohexene (**2**) were optimized by both molecular mechanics (force filed method) and quantum mechanical (MNDO method) calculations. Details will be reported in separate papers.[21,22] For the coplanar conformations shown in Figure 3 calculations by both MNDO and ab initio methods were carried out: similar results were obtained both for the ordering of π orbitals and the coefficients magnitudes. For the parent 1,4-benzoquinone as well as for compounds **1** and **2**, the experimental values of the first ionization potential and electron affinity, when available, are in generally good agreement with values calculated by MNDO method: so, the π orbital energies, coefficients, and net charges obtained by these calculations were used here.

Acknowledgment. We thank Dr. W. Porzio, CNR-ICM, Milan, for the collection of intensities with the PW 1100 diffractometer and Prof. K. N. Houk for helpful discussion. Financial support from the Italian CNR is gratefully acknowledged (Progetto Finalizzato per la Chimica Fine e Secondaria and Grant No. CT81.01684.03).

Registry No. **1**, 3958-79-0; **2**, 2622-21-1; **3**, 86309-53-7; **4**, 86309-54-8; **5**, 86309-55-9; **6**, 86309-56-0.

Supplementary Material Available: Tables listing the results of PMO calculations (Table I–III), energies and coefficients of the MNDO MO's of compounds **1** and **2** (Table IV), final coordinates and their estimated standard deviations for heavier atoms (Table V), coordinates for hydrogen atoms (Table VI), thermal parameters with their estimated standard deviations (Table VII), bond distances, bond angles, and selected torsion angles with their estimated standard deviations (Tables VIII–X) for product **5** (10 pages). Ordering information is given on any current masthead page.

(17) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *45*, 2091.
(18) Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 295.
(19) Wolfsberg, M.; Helmholz, L. *J. Chem. Phys.* **1952**, *20*, 837.
(20) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248.
(21) Pitea, D.; Moro, G. *J. Mol. Struct.*, in press.
(22) Pitea, D.; Moro, G.; Tantardini, G. F.; Todeschini, R. *J. Mol. Struct.*, in press.

Stereocontrolled Palladium(II)-Mediated Coupling of Furanoid Glycals with a Pyrimidinylmercuric Salt. Facile C-Nucleoside Syntheses

Uli Hacksell and G. Doyle Daves, Jr.*

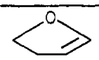
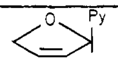
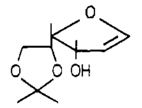
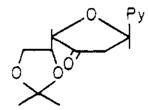
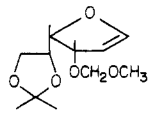
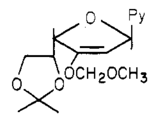
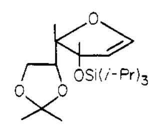
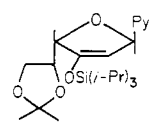
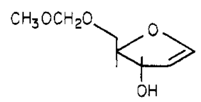
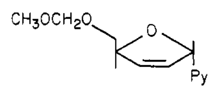
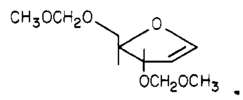
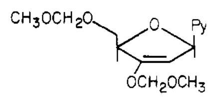
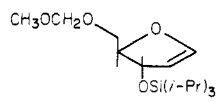
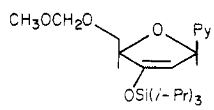
Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

Received January 7, 1983

Reactions of new, chiral furanoid glycals with (1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric acetate in the presence of a stoichiometric quantity of $Pd(OAc)_2$ resulted in regio- and stereospecific formation of α or β C-nucleosides. Results obtained demonstrate that preselection of the direction of attack by the organopalladium reagent on the cyclic enol ether double bond can be accomplished by adjustment of the relative steric bulks of the C_3 and C_4 substituents of trans-substituted furanoid glycals. With cis-substituted glycals, the attack occurs on the unsubstituted face of the ring.

Ongoing studies of the regio- and stereochemistry of palladium-mediated carbon–carbon bond forming reactions of cyclic enol ethers (glycals)[1,2] directed toward the development of a general synthesis of C-nucleosides[3,4] have

Table I. Reactions of Furanoid Glycals with (1,3-Dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric Acetate in the Presence of Stoichiometric Palladium(II) Acetate

glycal	product[a]	base (equiv)[b]	yield, %[c]
 2	 9		86[d]
 3	 10	$NaHCO_3$ (5)	49 63
 4	 11	$NaHCO_3$ (4)	56
 5	 12	$NaHCO_3$ (8.5)	88
 6	 13	 $NaHCO_3$ (3) $EtN(i\text{-}Pr)_2$ (2.4) K_2CO_3 (3)	35 75 78 30
 7	 14	$NaHCO_3$ (5)	71
 8	 15	 $NaHCO_3$ (5)	36 92

[a] Py = 1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl. [b] Base was added to the reaction mixture between 4 and 30 min after the addition of the glycal. [c] Isolated yield. [d] From ref 9.

now been extended to an investigation of furanoid glycals which, owing to greater conformational rigidity, possess certain advantages for the study of the stereochemistries of organometallic adduct-forming and decomposition reactions. New furanoid glycals have been prepared and converted selectively into α or β C-nucleosides. Results obtained in this study demonstrate that selection of the face of the cyclic enol ether experiencing attack by the organopalladium reagent can be accomplished by adjustment of the relative steric bulks of sustituents affecting access to the two respective faces of the furanoid ring.

Palladium-Mediated Reactions of Furanoid Glycals with (1,3-Dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric Acetate. Adduct Formation and Decomposition. Coupling between an olefin and an organomercuric salt in the presence of palladium(II), sometimes referred to as the "Heck reaction", proceeds via an initial transmetalation[5] leading to an organopalladium reagent which subsequently adds to the olefinic double bond in a syn fashion.[6] Finally, the intermediate organopalladium adduct thus formed decomposes, usually by an elimination process forming a new olefinic bond.[5] The adduct forming reaction, when applied to simple olefins, normally gives mixtures of regioisomers. However, with pyranoid glycals, which possess a highly polarized double bond,[8] the coupling is regiospecific[1] with the new carbon–carbon bond formed at the electron-deficient carbon bearing oxygen. Similarly, palladium(II)-mediated reaction

(1) (a) Arai, I.; Daves, G. D., Jr. *J. Org. Chem.* **1978**, *43*, 4110; (b) *J. Am. Chem. Soc.* **1978**, *100*, 287; (c) *Ibid.* *1981*, *103*, 7683; (d) Arai, I.; Lee, T. D.; Hanna, R.; Daves, G. D., Jr. *Organometallics* **1982**, *1*, 742.

(2) For related studies see Czernecki, S.; Gruy, F. *Tetrahedron Lett.* **1981**, *22*, 437; Dunkerton, L. V.; Serino, A. J. *J. Org. Chem.* **1982**, *47*, 2812.

(3) For recent reviews of the biology and chemistry of C-nucleosides see: Daves, G. D., Jr.; Cheng, C. C. *Prog. Med. Chem.* **1976**, *13*, 303. Hannessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *3*, 111. Fox, J. J.; Watanabe, K. A.; Klein, R. S.; Chu, C. K.; Tam, S. Y. K.; Reichman, U.; Hirota, K.; Wempen, I.; Lopez, Z.; Burchenal, J. H. *INSERM.* **1978**, *81*, 241.

(4) Noyori, R.; Sato, T.; Hayakawa, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2562. For another recent synthetic approach see: Schmidt, R. R., Hoffman, M. *Tetrahedron Lett.* **1982**, *23*, 409.

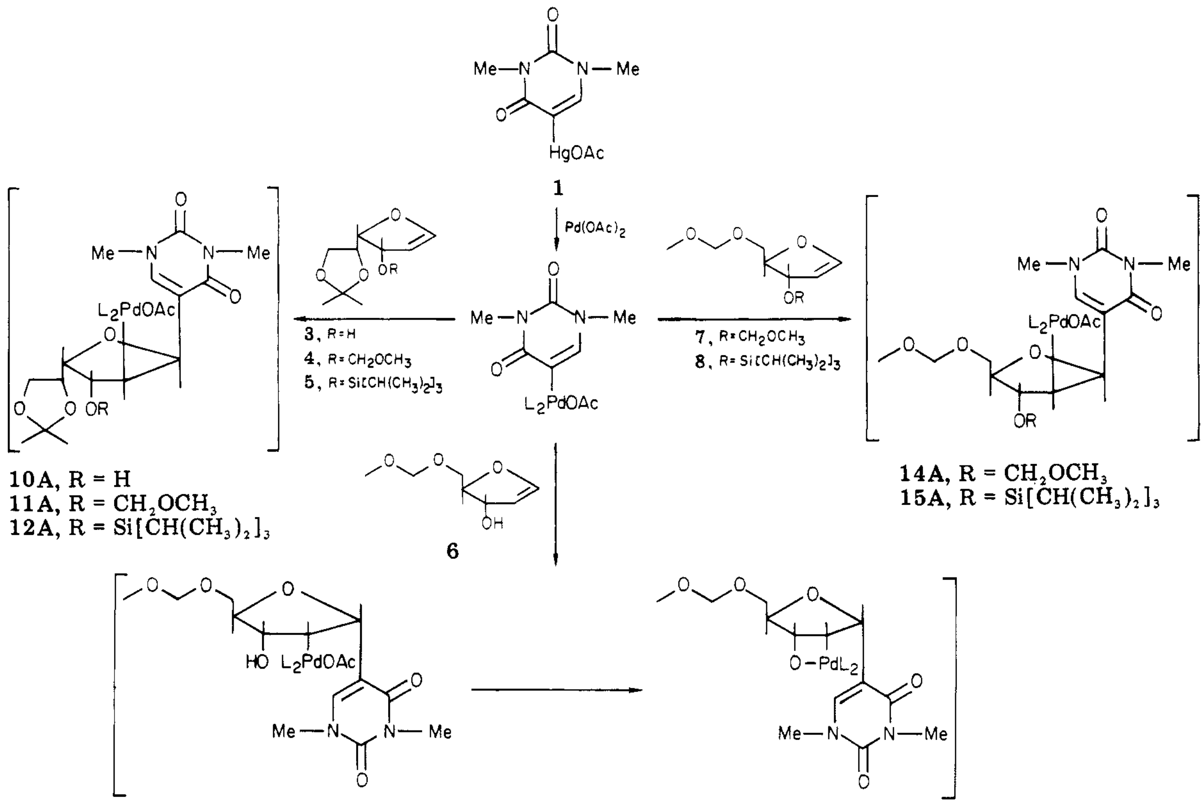
(5) For general reviews on palladium chemistry see: Henry, P. M. "Palladium Catalyzed Oxidation of Hydrocarbons"; Klewer Boston, Inc.: Boston, MA, 1980. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Velag: Berlin, 1980. Heck, R. F. "Organotransition Metal Chemistry", Academic Press: New York, 1974.

(6) All additions of organopalladium reagents to double bonds that have been carefully examined have been shown to be syn; no example of anti addition of carbon σ-bonded palladium reagent is known (see ref 5, 7). In our closely related studies using pyranoid glycals[1] syn addition of the palladium reagent derived from 1 has been established conclusively.

(7) (a) Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 673. (b) Bäckvall J. E., Åkermark, B.; Ljunggren, S. O. *Ibid.* **1979**, *101*, 2411. (c) Flood, T. C. In "Topics in Inorganic and Organometallic Stereochemistry"; Geoffrey, G., Ed.; Wiley: New York, 1981; Vol. 12, p 37.

(8) (a) Henrici-Olive, G.; Olive, S. *Top. Curr. Chem.* **1976**, *67*, 107; (b) Oakes, F. T.; Yang, F. A.; Sebastian, J. F. *J. Org. Chem.* **1982**, *47*, 3094.

Scheme I



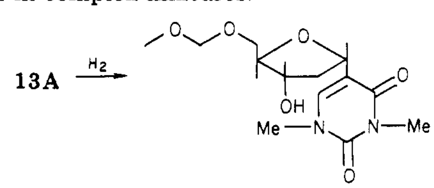
13A

of (1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric acetate (1)[1b] with 2,3-dihydrofuran (2) yielded a single product (9) produced by regiospecific coupling (Table I).[9]

In the present study this palladium-mediated coupling reaction has been extended to a number of chiral furanoid glycals (Table I). In each instance, organopalladium adduct formation was rapid at room temperature; thin layer chromatogrphic analyses showed that the furanoid glycal was consumed within 15 min. In contrast similar reactions of pyranoid glycals require several hours. Appearance of product was less rapid, indicating that the intermediate adducts are reasonably stable and under the reaction conditions decompose slowly. Although no adducts were isolated, formulation of their structures is straightforward based on product stereochemistries since adduct formation invariably involves syn addition[6] (see Scheme I).

Adduct **13A** is considerably more stable (cf. ref 1c) than the other palladium adducts prepared; decomposition of **13A** required heating at 70 °C or 8 h, whereas less stable adducts **11A**, **12A**, **14A**, and **15A**, decomposed within 4 h at room temperature. Addition of a weak base to the reaction mixtures, after adduct formation was complete, improved product yields (Table I). The presence of base accelerated the decomposition of adduct **13A**; decomposition occurred at room temperature when base was added.

The greater stability of **13A** made it possible to prepare 2-deoxy C-nucleoside[10] **16** in 76% yield by shaking a freshly prepared reaction mixture containing **13A** under hydrogen for 8 h. Preliminary attempts to prepare corresponding 2-deoxy C-nucleosides from reaction mixtures containing adducts **14A** or **15A**, using similar reaction conditions, resulted in complex mixtures.



16

Adducts **10A–12A**, **14A**, and **15A** decompose via syn elimination of hydridopalladium, a highly favored process.[5] For **13A**, no similarly facile mode of elimination is available; i.e., **13A** possesses no β-hydrogens cis to palladium[1c,d] and no acetoxy[1c,d] (or hydroxy)[7b] groups trans to palladium, and anti elimination of palladium alkoxide[1c,d] (opening of the furanoid ring) apparently does not occur in furanoid adducts owing to conformational constraints that inhibit attainment of the necessary anti periplanar configuration. Instead, adduct **13A** undergoes syn elimination of adjacent palladium and oxygen substituents.[11]

Stereochemistry of Adduct Formation. A principal objective of the present investigation was the determination of factors affecting the stereochemistry of syn addition of organopalladium reagent to the enol ether double bond, i.e., what controls which face of the double bond is attacked. The reactions of furanoid glycals possessing allylic alcohol functionality (**3**, **6**) were of particular interest because of the possibility that the allylic hydroxyl coordinates with the attacking palladium and thereby controls the stereochemistry of adduct formation.[12] Consistent with this possibility, reaction of **1** with **6** led to a product (**13**) resulting from organopalladium addition to the same face

(9) Lee, T. D.; Daves, G. D., Jr. *J. Org. Chem.* **1983**, *48*, 399.

(10) For convenience, we use the common carbohydrate numbering system (the anomeric carbon is designated 1′) in the running text and in the tables. Correct nomenclature can be found in the Experimental Section.

(11) Hacksell, U.; Daves, G. D., Jr. *Organometallics* **1983**, *2*, 772.

(12) (a) Heck, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6896; (b) *Org. React.* (*N.Y.*) **1982**, *27*, 345.

Table II. ^{13}C NMR of Furanoid Glycals[a]

compd	C_1	C_2	C_3	C_4	C_5	other
3	150.23	104.31	85.03	74.60[b]	73.73[b]	C_6 66.61 $C(CH_3)_2$ 109.78, 26.41, 25.43
4	150.51	101.65	85.78	78.25	74.56	C_6 66.65 $C(CH_3)_2$ 109.50, 26.67, 24.99 OCH_3 55.56, OCH_2O 94.72
6	149.00	102.90	87.05	74.84	67.17	OCH_3 54.73 OCH_2O 96.07
7	150.17	101.04	85.54	81.70	67.45	OCH_3's 55.42, 55.31 OCH_2O's 96.65, 95.35
8	148.84	103.60	87.83	76.11	67.44	OCH_3 55.11 OCH_2O 96.45 $CH(CH_3)_2$ 17.84, 12.10

[a] Values given in ppm and spectra run in $CDCl_3$. [b] Assignments could be reversed.

of the ring as occupied by the hydroxyl group (Scheme I). However, since in 6 the bulky substituent at C_4 and the C_3 hydroxyl group are on opposite faces, the observed stereochemistry could result from steric shielding of the nonhydroxyl bearing (β) face of the furanoid glycal. That steric effects are indeed dominant is evident from the result obtained in the palladium-mediated coupling of **1** with **3** in which the bulky C_4 substituent and the C_3 allylic hydroxyl group occupy the same face of the ring. In this reaction, the single coupled product observed (**10**) is that resulting from attack on the sterically open face of **3**.

These results indicated that selection of the direction of attack by organopalladium reagent might be accomplished by manipulation of the relative steric bulks of trans-disposed C_3 and C_4 substituents. Indeed, when allowed to react with **1** and $Pd(OAc)_2$, the 3-O-substituted glycals **7** and **8** gave adducts resulting from attack of the palladium reagent on the β-face of the glycal ring, i.e., anti to the α C_3 substituent which now shields the double bond from attack more effectively than the more remote β C_4 substituent on the opposite face of the ring. Thus, organopalladium attack occurs on the unsubstituted face when all ring substituents are cis (**3** → **10**, **4** → **11**, **5** → **12**) and on the least sterically shielded face when substituents are trans (**6** → **13**, **7** → **14**, **8** → **15**).

Comparison of Palladium-Mediated Reactions of Furanoid and Pyranoid Glycals. Some comparisons of reactions between palladium reagents and furanoid and pyranoid glycals are noteworthy: (a) Regiospecific attack of palladium reagent on furanoid and pyranoid glycals occurs consistently on the sterically least hindered face of the cyclic enol ether ring.[1] (b) Syn elimination of hydridopalladium dominates adduct decomposition for adducts derived from the furanoid glycals studied here (except for **13A**; see above[11]). Palladium adducts formed from the pyranoid glycals eliminate hydridopalladium but also decompose by anti eliminations of palladium acetate or of palladium alkoxide with concomitant ring opening.[1] (c) A mixture of products results from reaction between **1**, $Pd(OAc)_2$, and 3,4-dihydro-(2*H*)-pyran owing to double bond isomerization.[9] However, inspection of Table I shows no instance of similar double bond migration in palladium-mediated reactions of furanoid glycals.

Synthesis of Glycals. Recently, Ireland et al.[13] developed a general procedure for the synthesis of 3-hydroxylated, chiral glycals, involving as a key step the reductive fragmentation of a 2,3-*O*-isopropylidene-protected furanosyl or pyranosyl chloride. The method gives high yields of glycals after isolation using a combination of chromatography and distillition;[13] we obtained 1,4-anhydro-2-deoxy-5,6-*O*-(methylethylidene)-D-*xylo*-hex-1-enitol (**3**) and 1,4-anhydro-2-deoxy-5-*O*-(methoxymethyl)-D-*erythro*-pent-1-enitol (**6**)[13b] (Table I) in good yields after workup using repetitive flash chromatography.

During the course of our investigation we found it necessary to derivatize the allylic hydroxyl groups of furanoid glycal intermediates. Silylation of **3** and **6** using triisopropylsilyl chloride and imidazole in dry dimethylformamide[14] gave glycals **5** and **8**.[15] Similarly, alkylation of **3** and **6** with chloromethyl methyl ether and diisopropylethylamine in methylene chloride worked well, producing glycals **4** and **7** (Table I).[16]

Furanoid glycals exhibit characteristic ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra. In ^1H NMR spectra, H_1 and H_2 appear as doublets[18] ($J_{1,2} \sim 2.5$ Hz) at approximately δ 6.5 and 5.1, respectively. In ^{13}C NMR spectra, characteristic absorptions due to C_1 and C_2 occur at around δ 150 and 103 (Table II).

Structural Assignments of Products.[10] Detailed studies of ^1H and ^{13}C NMR (Table III) spectra and in two cases chemical correlations allowed structural assignments of compounds **9–16**. The ^1H NMR spectra of the 2′,3′-unsaturated C-nucleosides were analyzed by using first-order approximations when benzene-d_6 was used as solvent. Extensive spin-decoupling experiments allowed resonances of the different ring hydrogens to be assigned unambigously. For all compounds both proton noise decoupled and undecoupled ^{13}C NMR spectra were recorded.[19]

For establishing the relative configuration of ring substituents the most important factor in ^1H NMR spectra of compounds **11–15** is the long-range homoallylic coupling ($J_{1',4'}$). The empirically found trend, that trans homoallylic coupling constants always are larger than the corresponding cis couplings, has been rationalized theoretically by Barfield et al.[20] The large (5.8 Hz) $J_{1',4'}$ of **13** (Table

(13) (a) Ireland, R. E.; Wilcox, C. S.; Thaisrivongs, S. *J. Org. Chem.* **1978**, *43*, 786; (b) Ireland, R. E.; Thaisrivongs, S.; Vanier, N.; Wilcox, C. S. *Ibid.* **1980**, *45*, 48.

(14) Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797.

(15) *tert*-Butyldimethylsilylation of a 3-hydroxylated furanoid glycal has been reported previously: Corey, E. J.; Goto, G. *Tetrahedron Lett.* **1980**, 3463.

(16) 3-Alkoxy substituted furanoid glycals have been prepared previously in 6–25% yield using a modification of Fisher and Zach's method:[17] Bischofberger, K.; Hall, R. H., *Carbohydr. Res.* **1976**, *52*, 223.

(17) Ferrier, R. J. *Adv. Carbohydr. Chem.* **1965**, *20*, 67.

(18) $J_{1,3}$ is sometimes too small to be observed; cf. ref 13b.

(19) This was helpful, e.g., in the assignment of the singlet at 2.71 ppm in the ^1H NMR spectrum of **11**; the two N–Me's on the pyrimidine ring of **11** are easily distinguished in the undecoupled ^{13}C NMR spectrum. N_1-CH_3 appears as a quartet of doublets (36.18 ppm, J(C,H) = 141 Hz, J(C,N,C,H) = 3.8 Hz), whereas N_3-CH_3 appears as a quartet (27.40 ppm, J(C,H) = 141 Hz) without apparent splitting. Selective ^{13}C–[^1H] decoupling centered at 2.71 ppm shows collapse of the quartet at 36.18 ppm to a singlet. Thus, the singlet at 2.71 ppm is due to the N_1-Me.

(20) (a) Barfield, M.; Spear, R. J.; Sternhell, S. *J. Am. Chem. Soc.* **1971**, *93*, 5322; (b) Barfield, M.; Sternhell, S. *Ibid.* **1972**, *94*, 1905; (c) Barfield, M.; Spear, R. J.; Sternhell, S. *Ibid.* **1975**, *97*, 5160.

Table III. ^{13}C NMR of C-Nucleosides[a]

cmpd	solvent	N_1-CH_3	C_2	N_3-CH_3	C_4	C_5	C_6	C_1'	C_2'	C_3'	C_4'	C_5'	other
9	$CDCl_3$	36.86	151.64	27.54	161.01	114.37	138.98	81.23	128.25	126.44	75.21		
10	$CDCl_3$	37.00	151.37	27.68	162.25	113.28	140.19	74.78[b]	41.90	212.22	79.34[b]	75.71	C_6' 65.26; $C(CH_3)_2$ 109.72, 25.99, 25.34
11	C_6D_6	36.12	151.35	27.40	162.08	114.62	138.40	82.11[b]	98.96	151.84	80.17[b]	76.97	C_6' 65.70; $C(CH_3)_2$ 109.58, 26.37, 26.04; OCH_3 56.17; OCH_2O 95.98
12	C_6D_6	36.07	151.30	27.34	162.13	114.89	138.46	82.49[b]	101.18	150.65	80.38[b]	76.75	C_6' 66.02; $C(CH_3)_2$ 109.58, 26.42, 26.15; $SiCH(CH_3)_2$ 17.97, 12.55
13	$CDCl_3$	37.02	151.80	27.70	162.93	113.60	139.55	81.60	130.94	126.60	85.59	70.01	OCH_3 55.02; OCH_2O 96.69
	C_6D_6	36.18	151.85	27.40	162.13	113.70	138.75	82.06	131.12	127.19	85.83	70.44	OCH_3 54.95; OCH_2O 96.80
14	$CDCl_3$	36.97	151.71	27.65	162.49	115.08	140.17	81.28[b]	97.97	151.27	78.73[b]	68.01	OCH_3's 56.58, 55.22; OCH_2O's 46.56, 95.80
	C_6D_6	36.07	151.40[c]	27.34	162.29	115.11	139.48	81.84[b]	99.07	151.40[c]	79.62[b]	68.52	OCH_3's 56.06, 54.98; OCH_2O's 96.63, 95.88
15	C_6D_6	36.12	151.35	27.40	162.45	115.27	139.86	82.66[b]	101.89	150.16	78.92[b]	68.57	OCH_3 55.03; OCH_2O 96.69; $SiCH(CH_3)_2$ 17.92, 12.45
16	$CDCl_3$	36.97	151.46	27.81	162.60	113.49	140.76	73.98[b]	40.24	75.47[b]	85.66	68.14	OCH_3 55.22; OCH_2O 96.56

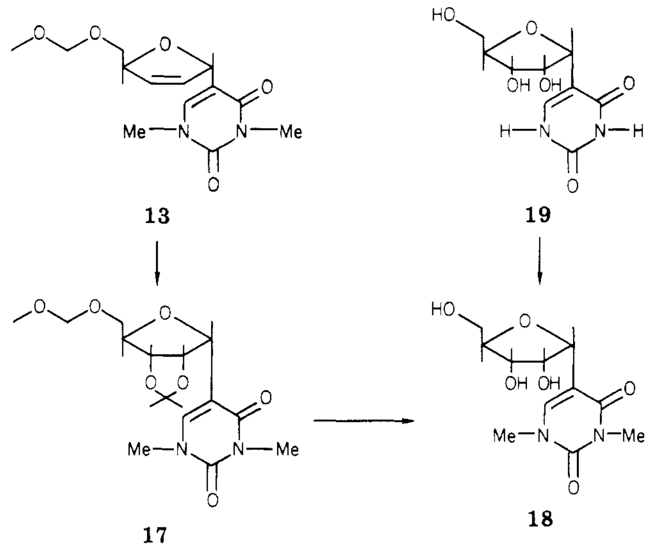
[a] Values given in ppm. [b] Assignments could be reversed. [c] Overlapping peaks.

Table IV. Homoallylic Coupling Constants Used for Stereochemical Assignments[a]

compd	$J_{1',4'}$, Hz cis	trans
11		5.3
12		5.3
13		5.8
14	3.0	
15	3.4	

[a] Recorded in benzene-d_6.

IV) is indicative of,[20,21] but does not establish,[22] a trans relationship between $H_{1'}$ and $H_{4'}$. Therefore, the stereochemistry of **13** was determined unambigously by its chemical conversion to 1,3-dimethyl-α-pseudouridine (**18**);[11] catalytic dihydroxylation of **13** using osmium tetroxide and trimethylamine *N*-oxide followed by isopropylidene protection gave **17**. Deprotection of **17** afforded **18**, which was identical with an authentic sample prepared from α-pseudouridine (**19**) by using *N*,*N*-dimethylformamide dimethyl acetal. The $J_{1',4'}$ values of 14



and **15** (Table IV) agree with calculated homoallylic coupling constants for 2,5-dihydrofuran using different pucker angles,[20c] assuming cis-pseudoaxial dispositions of $H_{1'}$ and $H_{4'}$ and a slightly larger puckering in **15** than in **14** due to the more severe steric crowding in **15**. Moreover, $J_{1',4'}$ in the closely related trans derivatives **11** and **12** is considerably larger than $J_{1',4'}$ in **14** and **15**, thus confirming the stereochemical assignments. The ^1H spectrum of **10** does not permit unambigous assignment of the configuration at $C_{1'}$. However, desilylation of **12** using tetrabutylammonium fluoride gave a product identical with **10**, thereby establishing the trans relationship between the $C_{1'}$ and $C_{4'}$ substituents of **10**.

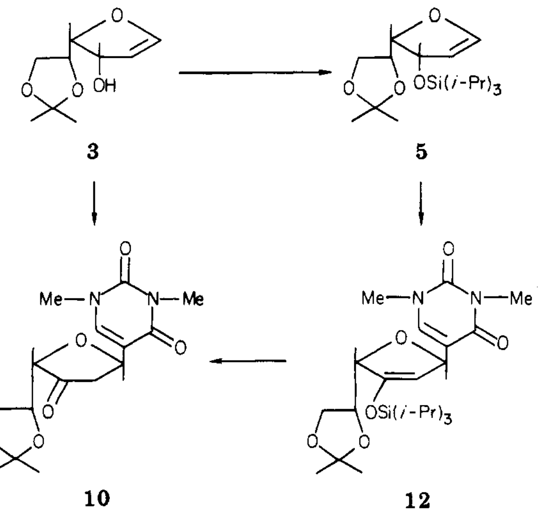
Concluding Remarks. The present and previous studies[1,9] demonstrate that coupling of palladium reagents with glycals is a remarkably selective reaction. In no in-

(21) $J_{1',4'}$ in 2′,3′-didehydro-2′,3′-dideoxy-1-methyl-5′-*O*-trityl-β-pseudouridine has been reported to be ~1.5 Hz in $CDCl_3$. Matsuda, A.; Chu, C. K.; Riechman, U.; Pankiewicz, K.; Watanbe, K. A.; Fox, J. J. *J. Org. Chem.* **1981**, *46*, 3603.

(22) Large cis homoallylic coupling constants have been reported for 2,5-dihydro-2-phenyl-5-(triphenylmethyl)furan[23] and for a series of 1,3-oxazoline derivatives.[24]

(23) Benati, L.; Tiecco, M.; Tundo, A.; Taddei, F. *J. Chem. Soc. B* **1970**, 1443.

(24) Giezendanner, H. von; Heimgartner, H.; Jackson, B.; Winkler, T.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2611.



stance has the formation of regio- or stereoisomers been observed. The regiospecificity of the reaction results from the polarization of the enolic double bond.[8,9] The extreme sensitivity of organopalladium adduct formation to the topology of the glycal, which makes it possible to synthesize compounds of differing stereochemistries by modifying the allylic substituent, is more difficult to rationalize.

Synthesis of a variety of C-nucleosides of potential biological interest can be envisaged from compounds such as **14** and **15**.[3] Especially attractive is the possibility of manipulating separately $C_{3'}$ and $C_{5'}$ substituents of **15** after selective deblocking.

Experimental Section

General Comments. Chemicals were used as received except for tetrahydrofuran, which was distilled from lithium aluminum hydride under nitrogen. Thin-layer chromatography (TLC) was carried out on prescored silica gel GF plates (Analtech). Preparative TLC was carried out on 1 mm thick, 20 × 20 cm, silica gel GF plates (Analtech). For flash chromatography, silica gel 60 (230–400 mesh ASTM, E. Merck) was used. Columns were eluted using a positive nitrogen pressure. NMR spectra were obtained on a JEOL FX 90Q spectrometer and were referenced to tetramethylsilane. Coupling constants were measured on expanded spectra obtained from degassed samples. Mass spectra were obtained with a Finnegan 4023 GC/MS/DS system operating at 70 eV using a direct insertion probe. Elemental analyses were carried out by Dr. G. Robertson, Florham Park, NJ.

Preparation of Glycals. 1,4-Anhydro-2-deoxy-5,6-*O*-(1-methylethylidene)-D-*xylo*-hex-1-enitol (3). By use of the method of Ireland et al.,[13] 10.08 g (38.4 mmol) of 2,3:5,6-di-*O*-(1-methylethylidene)-D-*gulo*-furanose[25] was reacted with 8.2 mL (38.4 mmol) of hexamethylphosphoric triamide (85%) and 4.5 mL (46.6 mmol) of dry carbon tetrachloride in 50 mL of dry tetrahydrofuran. The resulting solution was reacted with lithium (3.25 g, 468 mmol) in ammonia (600 mL). After addition of ammonium chloride (25.5 g, 477 mmol) and ether to the reaction mixture, the ammonia was allowed to evaporate. Addition of magnesium sulfate to the resulting suspension followed by filtration and evaporation of volatiles in vacuo gave an oil which was subjected to repetitive flash chromatography first with ether as eluant and then twice with 1:1 ether/petroleum ether. Combination of pure fractions gave a total yield of 6.4 g (76%) of **3**: ^{1}H NMR ($CDCl_3$) 6.61 (d, J = 2.6 Hz, H_1), 5.21 (t, J = 2.6 Hz, H_2), 4.82 (dt, J_1 = 9 Hz, J_2 = 2.6 Hz, H_3), 4.65–4.08 (m, 3 H), 3.84 (dd, J_1 = 9.7 Hz, J_2 = 6.6 Hz, H_4), 2.59 (d, J = 9 Hz, OH) 1.45, 1.39 (s's, Me's); mass spectrum, m/z 186 (16%, $M^{+\cdot}$), 171 (45%, $M^{+\cdot} - CH_3$), 153 (22%, $M^{+\cdot} - CH_3 - H_2O$). Anal. Calcd for $C_9H_{14}O_4$: C, 58.0; H, 7.58. Found: C, 57.2; H, 7.60.

1,4-Anhydro-2-deoxy-3-*O*-(methoxymethyl)-5,6-*O*-(1-methylethylidene)-D-*xylo*-hex-1-enitol (4). To a precooled solution (ice bath) of **3** (530 mg, 2.84 mmol) and diisopropylethylamine (3.87 g, 28.4 mmol) in dry methylene chloride (15 mL) was added carefully a solution of chloromethyl methyl ether (914 mg, 11.36 mmol) in dry methylene chloride (10 mL). The mixture was stirred for 24 h at room temperature under nitrogen. The volatiles were evaporated in vacuo and the residual oil was dissolved in methylene chloride (2 mL) and applied on a silica column. Flash chromatography using ether/petroleum ether 1:1 as eluant gave 498 mg (76%) of pure **4** as an oil: ^{1}H NMR ($CDCl_3$) δ 6.60 (d, J = 2.6 Hz, H_1), 5.24 (t, J = 2.6 Hz, H_2), 5.85–4.07 (m, 6 H), 3.69 (dd, J_1 = 8.4 Hz, J_2 = 6.4 Hz, H_4), 3.31 (s, OMe), 1.45, 1.36 (s's, Me's). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.4; H, 7.88. Found: C, 57.1; H, 7.88.

1,4-Anhydro-2-deoxy-5-*O*-(methoxymethyl)-D-*erythro*-pent-1-enitol (6).[13b] The method of Ireland[13] was followed; however, purification of crude **6** was achieved by using repetitive flash chromatography as described above for the purification of **3**. This procedure gave a pure product, which was stable for several months when kept at −5 °C under N_2.

1,4-Anhydro-2-deoxy-5,3-bis-*O*-(methoxymethyl)-D-*erythro*-pent-1-enitol (7). Compound **7** was prepared from **6** (480 mg, 3 mmol) by use of the procedure described for the preparation of **4**. Flash chromatography of the crude product using ether/petroleum ether 1:3 as eluant gave 546 mg (89%) of pure **7** as an oil: ^{1}H NMR ($CDCl_3$) δ 6.56 (dd, $J_{1,2}$ = 2.5 Hz, $J_{1,3}$ = 1 Hz, H_1), 5.14 (dd, $J_{2,3}$ = 2.6 Hz, H_2), 4.86–4.82 (m, partially obscured, H_3, H_4), 4.69, 4.66 (s's, OCH_2O's), 3.60 (d, J = 5.7 Hz, H_5, $H_{5'}$), 3.37 (s, OMe's). Anal. Calcd for $C_9H_{16}O_5$: C, 52.9; H, 7.90. Found: C, 53.0; H, 7.74.

1,4-Anhydro-2-deoxy-5-*O*-(methoxymethyl)-3-*O*-[tris(1-methylethyl)silyl]-D-*erythro*-pent-1-enitol (8). By use of the procedure of Cunico and Bedell[14] 450 mg (2.33 mmol) of triisopropylsilyl chloride was added to a solution of **6** (311 mg, 1.94 mmol) and imidazole (330 mg, 4.85 mmol) in 1 mL of dry dimethylformamide under nitrogen. After 2 h, TLC indicated that the reaction was complete and the reaction mixture was applied on a silica column. Flash chromatography using ether/petroleum ether 1:1 as eluant gave, after evaporation in vacuo, 700 mg of an oil containing the silylated glycal **8** and triisopropylsilanol (NMR analysis indicated that these products were obtained in an 8:2 ratio). This mixture was used without further purification. An analytical sample was purified by flash chromatography of the mixture using ether/petroleum ether 1:9 as eluant: NMR ($CDCl_3$) δ 6.50 (dd, $J_{1,2}$ = 2.5 Hz, $J_{1,3}$ = 1 Hz, H_1), 5.09 (dd, $J_{2,3}$ = 2.5 Hz, H_2), 4.91 (ddd, $J_{3,4}$ = 3.1 Hz, H_3), 4.66 (s, OCH_2O), 4.45 (dt, $J_{4,5}$ = 5.7 Hz, H_4), 3.58 (d, H_5, $H_{5'}$), 3.37 (s, OMe), 1.05 (m, $SiCH(CH_3)_2$'s). Anal. Calcd for $C_{16}H_{32}O_4Si$: C, 60.7; H, 10.20. Found: C, 61.0; H, 10.34.

Palladium-Mediated Reactions of Furanoid Glycals. Below are given representative examples of the reactions presented in Table I.

5-[2′-Deoxy-5′,6′-*O*-(1-methylethylidene)-β-D-*threo*-hexofurano-3′-ulos-1′-yl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (10). To a 25-mL vial equipped with a screw lid and a stirring bar were added $Pd(OAc)_2$ (202 mg, 0.9 mmol), (1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)mercuric acetate (**1**)[1b] (360 mg, 0.9 mmol), and acetonitrile (10 mL). The mixture was stirred for 5 min. To the resulting dark solution was added a solution of **3** (188 mg, 1.01 mmol) in acetonitrile (5 mL). After 2 days the reaction mixture was filtered through glass wool and volatiles were evaporated in vacuo. Flash chromatography (using ethyl acetate as eluant) of the dark residue followed by preparative TLC (ethyl acetate) of partially purified **10** afforded 141 mg (49%) of pure **10** as an oil and 85 mg of an impure fraction (NMR analysis indicated a 1:1 mixture of **10** and dimethyluracil). Crystallization of **10** was accomplished by trituration with a small amount of ether: mp 127–128 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (d, J = 0.8 Hz, H_6), 5.28 (m, $H_{1'}$), 4.49–3.95 (m, 4 H), 3.43, 3.34 (s's, NMe's), 3.18–2.38 (m, $H_{2'}$, $H_{2''}$), 1.44, 1.35 (s's, Me's). Anal. Calcd for $C_{15}H_{20}N_2O_6$: C, 55.6; H, 6.22; N, 8.64. Found: C, 55.7; H, 6.19; N, 8.58.

5-[2′-Deoxy-3′-*O*-(methoxymethyl)-5′,6′-*O*-(1-methylethylidene)-β-D-*threo*-hex-2′-enofuranosyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (11). A mixture of $Pd(OAc)_2$ (179 mg, 0.8 mmol), **1** (318 mg, 0.8 mmol), and **4** (220 mg, 0.96 mmol) in acetonitrile (15 mL) was prepared by using the procedure

(25) Hulyalkar, R. K. Can. J. Chem. 1966, 44, 1594.

described for the preparation of **10**. Ten min after the addition of **4**, sodium carbonate (276 mg, 3.18 mmol) was added to the reaction mixture. After 2 h the mixture was filtered through glass wool and the volatiles were evaporated. Flash chromatography (using ether as eluant) gave 148 mg (56%) of pure **11** as an oil. ^{1}H NMR (C_6D_6) δ 6.73 (d, J = 1.25 Hz, H_6), 5.94 (ddd, $J_{1',2'}$ = 1.65 Hz, $J_{1',4'}$ = 5.3 Hz, $H_{1'}$), 5.40 (t, J = 1.65 Hz, $H_{2'}$), 4.90–3.87 (m, 6 H), 3.19, 3.09, 2.64 (s's, OMe, NMe's), 1.46, 1.36 (s's, Me's). Anal. Calcd for $C_{17}H_{24}N_2O_7$: C, 55.4; H, 6.57; N, 7.60. Found: C, 55.2; H, 6.66; N, 7.33.

5-[2′-Deoxy-5′,6′-*O*-(1-methylethylidene)-3′-*O*-[tris(1-methylethyl)silyl]-*β*-D-*threo*-hex-2′-enofuranosyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (12). By use of the procedure of Cunico and Bedell[14] 2.29 g (11.88 mmol) of triisopropylsilyl chloride was added to a solution of **3** (1.578 g, 8.48 mmol) and imidazole (1.444 g, 21.21 mmol) in dry dimethylformamide. After 24 h at room temperature the reaction mixture was applied on a silica column. Flash chromatography using ether/petroleum ether 1:1 gave an oil which was rechromatographed (ether/petroleum ether 1:9), affording 1.965 g of a mixture of 1,4-anhydro-2-deoxy-5,6-*O*-(1-methylethylidene)-3-*O*-[tris(1-methylethyl)silyl]-D-*xylo*-hex-1-enitol (**5**) and 2-[1,2-*O*-(1-methylethylidene)-1,2-dihydroxyethyl]furan (NMR analysis indicated that these products were obtained in a 1:1 ratio); 600 mg (0.93 mmol of **4**) of this mixture was then added to a preprepared mixture of $Pd(OAc)_2$ (157 mg, 0.70 mmol), **1** (279 mg, 0.70 mmol), and acetonitrile (50 mL). After 15 min sodium bicarbonate (500 mg, 5.95 mmol) was added to the black slurry and the reaction mixture was stirred overnight. Filtration (Celite) and evaporation of the volatiles in vacuo gave an oil which was purified using flash chromatography (ether) to afford 297 mg (88%) of pure **12**: ^{1}H NMR (C_6D_6) δ 6.81 (d, J = 1.2 Hz, H_6), 5.94 (ddd, $J_{1',2'}$ = 1.6 Hz, $J_{1',4'}$ = 5.3 Hz, $H_{1'}$), 5.30 (t, J = 1.7 Hz, $H_{2'}$), 4.60–3.90 (m, 4 H), 3.16, 2.64 (s's, NMe's), 1.46, 1.36 (s's, Me's), 1.03 (narrow m, $SiCH(CH_3)_2$'s).

(2′*S*)-*trans*-5-[2′,5′-Dihydro-5′-[(methoxymethoxy)-methyl]-2′-furanyl]-1,3-dimethyl-2,4-pyrimidinedione (13). A mixture of $Pd(OAc)_2$ (45 mg, 0.2 mmol), **1** (80 mg, 0.2 mmol), and **6** (40 mg, 0.25 mmol) in acetonitrile (15 mL) was prepared using the procedure described for the preparation of **10**. After 5 min, diisopropylethylamine (80 mg, 0.6 mmol) was added and the reaction mixture was stirred at room temperature for 3 days. Filtration through glass wool and evaporation of the volatiles in vacuo gave a dark oil which was purified using preparative TLC (ethyl acetate). Rechromatography (preparative TLC, ethyl acetate) of slightly impure **13** gave 44 mg (78%) of pure **13** as an oil: ^{1}H NMR (C_6D_6) δ 6.84 (d, J = 1.25 Hz, H_6), 6.24 (ddd, $J_{2',3'}$ = 5.95 Hz, $J_{2',4'}$ = −2.0 Hz, $H_{2'}$), 5.87 (dddd, $J_{1',2'}$ = 1.6 Hz, $J_{1',3'}$ = 2.25 Hz, $J_{1',4'}$ = 5.8 Hz, $H_{1'}$), 5.67 (ddd, $J_{3',4'}$ = 1.6 Hz, $H_{3'}$), 5.06 (dddt, $J_{4',5'}$ = 5.2 Hz, $H_{4'}$), 4.58 (s, OCH_2O), 3.57 (d, $H_{5'}$, $H_{5''}$), 3.24, 3.22, 2.71 (s's, OMe, NMe's); mass spectrum, m/z 282 (3%, $M^{+\cdot}$), m/z 251 (4%, $M^{+\cdot}$ − CH_3O), m/z 207 (80%, $M^{+\cdot}$ − $CH_3OCH_2OCH_2$). Anal. Calcd for $C_{13}H_{18}N_2O_5$: C, 55.3; H, 6.43; N, 9.92. Found: C, 54.8; H, 6.28; N, 9.34.

(2′*R*)-*cis*-5-[2′,5′-Dihydro-5′-[(methoxymethoxy)-methyl]-4′-(methoxymethoxy)-2′-furanyl]-1,3-dimethyl-2,4-(1*H*,3*H*)-pyrimidinedione (14). A mixture of **7**, (102 mg, 0.5 mmol), **1** (160 mg, 0.4 mmol), $Pd(OAc)_2$ (90 mg, 0.4 mmol), sodium bicarbonate (170 mg, 2 mmol), and acetonitrile (15 mL) was prepared by using the procedure described for the preparation of **11**. After 24 h the reaction mixture was filtered through glass wool and the volatiles were evaporated in vacuo. Preparative TLC (ether) gave 97 mg (71%) of **14**: mp 116–117 °C; ^{1}H NMR (C_6D_6) δ 7.21 (d, J = 1.25 Hz, H_6), 6.02 (ddd, $J_{1',2'}$ = 1.65 Hz, $J_{1',4'}$ = 2.95 Hz, $H_{1'}$), 5.38 (dd, $J_{2',4'}$ = −1.8 Hz, $H_{2'}$), 4.88–4.70 (m, $H_{4'}$), 4.70–4.35 (ABm's, OCH_2O's), 4.03–3.52 (m, $H_{5'}$, $H_{5''}$), 3.20, 3.12, 3.04, 2.71 (s's, OMe's, NMe's). Anal. Calcd for $C_{15}H_{22}N_2O_7$: C, 52.6; H, 6.48; N, 8.18. Found: C, 52.4; H, 6.53; N, 7.92.

(2′*R*)-*cis*-5-[2′,5′-Dihydro-5′-[(methoxymethoxy)-methyl]-4′-[[tris(1-methylethyl)silyl]oxy]-2′-furanyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (15). A mixture of **8** (83%; 257 mg, 0.67 mmol), **1** (214 mg, 0.54 mmol), $Pd(OAc)_2$ (120 mg, 0.54 mmol), sodium bicarbonate (225 mg, 2.68 mmol), and acetonitrile (25 mL) was prepared by using the procedure described for the preparation of **11**. After 3 h the reaction mixture was filtered through glass wool and the volatiles were evaporated in vacuo. Flash chromatography (ether/petroleum ether 1:1) followed by preparative TLC (ether/petroleum ether 1:1) gave 234 mg (92%) of pure **15**: ^{1}H NMR (C_6D_6) δ 7.32 (d, J = 1.2 Hz, H_6), 6.02 (ddd, $J_{1',2'}$ = 1.7 Hz, $J_{1',4'}$ = 3.4 Hz, $H_{1'}$), 5.28 (dd, $J_{2',4'}$ = −1.8 Hz, $H_{2'}$), 4.95–4.55 (m, 3 H), 3.95–3.55 (m, $H_{5'}$, $H_{5''}$), 3.20, 3.16, 2.73 (s's, OMe, NMe's), 1.05 (narrow m, $SiCH(CH_3)_2$'s). Anal. Calcd for $C_{22}H_{38}N_2O_6Si$: C, 58.1; H, 8.42; N, 6.16. Found: C, 58.0; H, 8.69; N, 6.03.

Hydrogenolysis of Intermediate 13A: Preparation of 5-[2′-Deoxy-5′-*O*-(methoxymethyl)-*α*-D-*erythro*-pentofuranosyl]-1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione (16). To a solution of bis(acetonitrilo)palladium(II) acetate (prepared by stirring a mixture of $Pd(OAc)_2$ (75 mg, 0.33 mmol), acetonitrile (0.035 mL, 0.67 mmol), and tetrahydrofuran (1 mL) for 2 days at room temperature) were added tetrahydrofuran (20 mL) and **1** (133 mg, 0.33 mmol). After 10 min glycal **6** (80 mg, 0.50 mmol) was added and the resulting reddish suspension was stirred in a hydrogenation bottle until it became homogeneous and completely black (70 min). The reaction mixture was then shaken under hydrogen (35 psi) for 8 h. Filtration (Celite) of the black precipitate and evaporation of volatiles in vacuo afforded 245 mg of an oil which was purified using preparative TLC (ethyl acetate/methanol 20:1). Rechromatography of a partially purified fraction (preparative TLC; ethyl acetate/ether 1:1) gave 75 mg (76%) of **16** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.33 (unresolved d, H_6), 4.85 (m, $H_{1'}$), 4.65 (s OCH_2O), 4.28 (m, $H_{3'}$, $H_{4'}$), 3.59 (d, J = 4.8 Hz, $H_{5'}$, $H_{5''}$), 3.41, 3.37, 3.34 (s's, OMe, NMe's), 2.90–1.85 (ABm, $H_{2'}$, $H_{2''}$); Mass spectrum, m/z 300 (3%, $M^{+\cdot}$), 255 (6%, $M^{+\cdot}$ − CH_3OCH_2), 207 (25%, $M^{+\cdot}$ − $CH_3OCH_2OCH_2$ − H_2O). Anal. Calcd for $C_{13}H_{20}N_2O_6$: C, 52.0; H, 6.71; N, 9.33. Found: C, 51.7; H, 6.69; N, 9.12.

Desilylation of 12: Alternative Preparation of 10. To a precooled (−78 °C) solution of **12** (113 mg, 0.24 mmol) and acetic acid (16 mg, 0.26 mmol) in tetrahydrofuran (30 mL) was slowly added 0.23 mL of a 1 M solution of tetrabutylammonium fluoride in tetrahydrofuran. After 30 min more acetic acid (16 mg) was added and the cooling was discontinued. Evaporation of volatiles in vacuo followed by preparative TLC (ethyl acetate gave 73 mg (95%) of **10**, identical with the product resulting from the Pd-$(OAc)_2$-mediated reaction of **1** and **3** (see above).

Acknowledgment. Financial support of this work from the National Institute of General Medical Science (Grant GM 30310), from S. Söderlundhs Minnesford, and from Thuns fond is greatly appreciated. We thank Robert A. Outten and Jane Chi-Ya Cheng for help with the synthetic experiments and William R. Anderson for help with NMR and mass spectrometry.

Registry No. **1**, 65904-27-0; **3**, 86495-11-6; **4**, 86436-79-5; **5**, 86455-84-7; **6**, 72050-15-8; **7**, 86436-80-8; **8**, 86436-81-9; **10**, 86436-82-0; **11**, 86436-83-1; **12**, 86455-83-6; **13**, 85442-29-1; **14**, 86455-85-8; **15**, 86436-84-2; **16**, 85442-26-8; $Pd(OAc)_2$, 3375-31-3; 2,3:5,6-di-*O*-(1-methylethylidene)-D-*gulo*-furanose, 13199-23-0; 2-[1,2-*O*-(1-methylethylidene)-1,2-dihydroxyethyl]furan, 19377-76-5.