Vinyl Radical-Based Cyclization of 6-Substituted 1-(2-Deoxy-D-*erythro*-pent-1-enofuranosyl)uracils: Synthesis of Anomeric Spiro Nucleosides[1]

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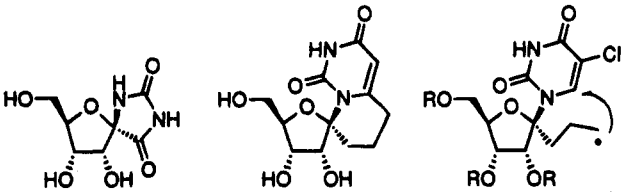
The preparation of 6-bromovinyl derivatives of 1-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)uracils (**10-13**) and their radical-mediated reactions leading to the formation of cyclized products were investigated with the aim of developing a new method for the synthesis of anomeric spiro nucleosides. Treatment of O^2,2′-anhydrouridine **5** with LDA followed by HCO_2Me gave 1-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)-6-formyluracil (**9**). The 6-bromovinyl derivatives **10-13** were prepared by Wittig reaction of **9**. Compounds **10**, **12**, and **13** underwent a vinyl radical-mediated cyclization (Bu_3SnH/AIBN, in refluxing benzene) preferentially in a 5-*exo-trig* manner to give 2′-deoxy-6,1′-ethenouridines **14a** and **17** and the corresponding α-anomers **15a** and **18** with preponderance of the former. The anomeric stereochemistry of these spiro nucleosides was unambiguously determined based on X-ray crystallography and their chemical reactions. Conversion of **14a** to 2′-deoxy-6,1′-ethanouridine (**26**) was also carried out. The present method offers a straightforward synthesis of certain anomeric spiro nucleosides.

Introduction

The isolation of hydantocidin (**1**)[2] from the culture broth of *Streptomyces hygroscopicus* SANK 63584 stimulated the synthesis of this class of compounds due to its unique anomeric spiro structure as well as its herbicidal and plant-growth regulatory activities.[3-5] When the anomeric spiro structure is included into naturally occurring nucleosides, such molecules are expected to serve as conformationally fixed models which can be useful to elucidate the glycosidic torsion angle of nucleosides.

In this context, Yoshimura *et al.* recently reported the synthesis of 6,1′-propanouridine (**2**) from D-fructose, wherein nucleophilic addition of an alkyl radical generated in the 1′-side chain was used as a key step, which had taken place at the electron-deficient C-6 position as depicted in **3**.[6] However, the usefulness of this approach is apparently limited by the number of steps required to achieve the conversion of D-fructose to the 1′-branched radical precursor.



1 **2** **3**

R = protecting group

During the course of our studies on lithiation chemistry of uridine derivatives,[7] 2′-deoxy-2′-fluorouridine (**4**) was reacted with LDA to give 1-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)uracil (**7**) as shown in Scheme 1.[8] When the lithiated reaction mixture was quenched with CH_3OD, exclusive C-6 deuteration occurred to give **8** (79% deuterium incorporation). The formation of **7** can be assumed to be the result of two consecutive reactions, an intramolecular nucleophilic displacement to give **5**, followed by β-elimination leading to **6**, based on the fact that the LDA treatment of the O^2,2′-anhydrouridine **5** and successive quenching with CH_3OD gave **8**, with much the same extent of deuterium incorporation at the C-6 position (74%).[9]

We considered **6** would serve as an excellent species for a straightforward synthesis of anomeric spiro nucleosides, since its 1′,2′-double bond can act as a radical acceptor and also its reaction with an appropriate electrophile may allow the introduction of a C-6 side chain, from which

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(1) This paper is dedicated to Dr. Morio Ikehara on the occasion of his 70th birthday.

(2) (a) Haruyama, H.; Takayama, T.; Kinoshita, T.; Kondo, M.; Nakajima, M.; Haneishi, T. *J. Chem. Soc. Perkin Trans. 1* **1991**, 1637–1640. (b) Nakajima, M.; Itoi, K.; Takamatsu, Y.; Kinoshita, T.; Okazaki, T.; Kawakubo, K.; Shindo, M.; Honma, T.; Tohjigamori, M.; Haneishi, T. *J. Antibiot.* **1991**, *44*, 293–300.

(3) For the synthesis of **1** and its stereoisomers: (a) Mio, S.; Ichinose, R.; Goto, K.; Sugai, S.; Sato, S. *Tetrahedron* **1991**, *47*, 2111–2120. (b) Mio, S.; Shiraishi, M.; Sugai, S.; Haruyama, H.; Sato, S. *Ibid.* **1991**, *47*, 2121–2132. (c) Mio, S.; Kumagawa, Y.; Sugai, S. *Ibid.* **1991**, *47*, 2133–2144. (d) Mio, S.; Ueda, M.; Hamura, M.; Kitagawa, J.; Sugai, S. *Ibid.* **1991**, *47*, 2145–2154. (e) Fairbanks, A. J.; Ford, P. S.; Watkin, D. J.; Fleet, G. W. J. *Tetrahedron Lett.* **1993**, *34*, 3327–3330. (f) Matsumoto, M.; Kirihara, M.; Yoshino, T.; Katoh, T.; Terashima, S. *Tetrahedron Lett.* **1993**, *34*, 6289–6292. (g) Chemla, P. *Ibid.* **1993**, *34*, 7391–7394.

(4) For other ribofuranose derivatives having an anomeric spiro structure: (a) Ferris, J. P.; Devadas, B. *J. Org. Chem.* **1987**, *52*, 2355–2361. (b) Yokoyama, M.; Yamada, N. *Tetrahedron Lett.* **1989**, *30*, 3675–3676. (c) Yokoyama, M.; Yamada, N.; Togo, H. *Chem. Lett.* **1990**, 753–756.

(5) Glycosidic spiro orthoesters have been synthesized based on homolysis of the anomeric C–H bond: (a) Praly, J.-P.; Descotes, G. *Tetrahedron Lett.* **1982**, *23*, 849–852. (b) Praly, J.-P.; Descotes, G.; Grenier-Loustalot, M.-F.; Metras, F. *Carbohydr. Res.* **1984**, *128*, 21–35. (c) Praly, J.-P.; Boyé, S.; Joseph, B.; Rollin, P. *Tetrahedron Lett.* **1993**, *34*, 3419–3420.

(6) Yoshimura, Y.; Otter, B. A.; Ueda, T.; Matsuda, A. *Chem. Pharm. Bull.* **1992**, *40*, 1761–1769.

(7) For a review article: Tanaka, H.; Hayakawa, H.; Miyasaka, T. In *Nucleosides and Nucleotides as Antitumor and Antiviral Agents*; Chu, C. K., Baker, D. C., Eds.; Plenum Press: New York, 1993; pp 23–53.

(8) Kittaka, A.; Tanaka, H.; Miyasaka, T.; Yamaguchi, K. *Nucleosides Nucleotides* **1992**, *11*, 37–47.

(9) For the preparation of **7** from **5**: (a) Robins, M. J.; Trip, E. M. *Tetrahedron Lett.* **1974**, 3369–3372. (b) Haraguchi, K.; Tanaka, H.; Maeda, H.; Itoh, Y.; Saito, S.; Miyasaka, T. *J. Org. Chem.* **1991**, *56*, 5401–5408.

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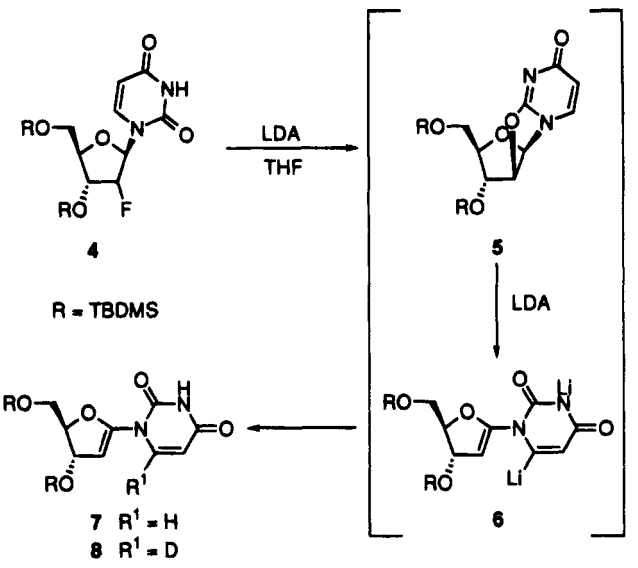
Scheme 1

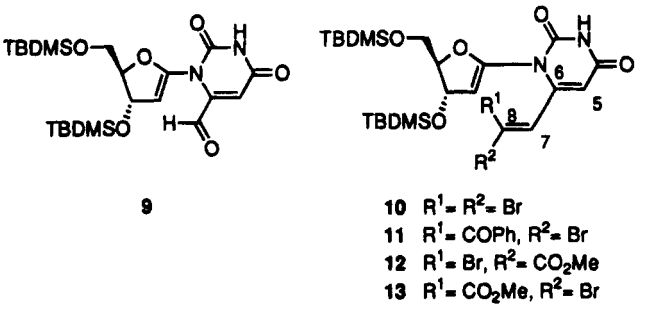


predictable radicals can be generated. In this article, we describe the preparation of 6-bromovinyl derivatives of 1-(2-deoxy-D-*erythro*-pent-1-enofuranosyl)uracil and their radical-based 5-*exo-trig* cyclization leading to anomeric spiro nucleosides.

Preparation of 6-Bromovinyl Derivatives of 1-(2-Deoxy-D-*erythro*-pent-1-enofuranosyl)uracil. Introduction of bromovinyl groups to the C-6 position of **7** was initiated by reacting HCO_2Me with **6**, which yielded the 6-formyl derivative **9**. Subsequent Wittig reaction of **9** furnished the desired vinyl radical precursors. Thus, **5** was treated with LDA (3 equiv) in THF at −78 °C for 15 min and the reaction mixture containing **6** was quenched with HCO_2Me (11 equiv). After partial purification by short column chromatography on silica gel, the resulting **9**[10] was reacted with an appropriate phosphorane, Ph_3PCBr_2,[11] $Ph_3PC(Br)COPh$, and $Ph_3PC(Br)CO_2Me$, to give **10** (54.3% yield, in DMF/CH_2Cl_2), **11** (25.8% yield, in THF),[12] and **12** plus **13** (*ca.* 2.5:1, total yield 50.1%, in DMF), respectively.

The above-prepared **12** and **13** were separated by column chromatography and their configurations about the vinyl moiety were determined on the basis of the following ^1H NMR observations: the vinyl proton (H-7) of **12** appeared at δ 7.74 ppm as a doublet (J = 1.1 Hz), which is significantly deshielded when compared to that of **13** (δ 6.97 ppm, J = 1.1 Hz), due to the anisotropic effect of the methoxycarbonyl group.[13] In contrast to this, **11** (H-7, δ 7.18 ppm, J = 1.1 Hz) was obtained as the sole product.

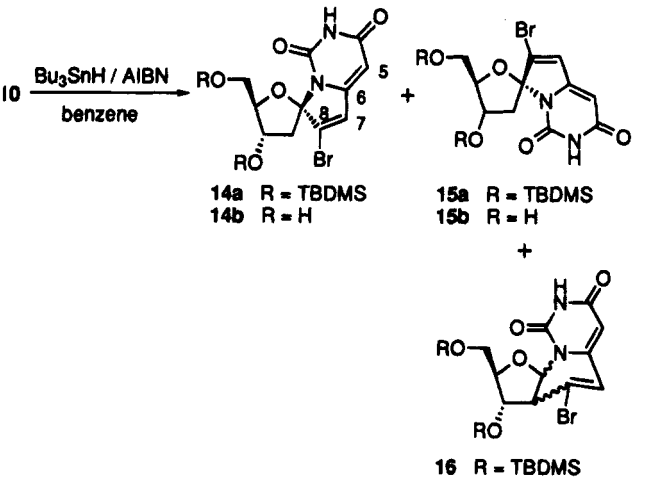
Radical Cyclization of the 6-Bromovinyl Derivatives 10−13. Since Stork's pioneering work on vinyl radical cyclization,[14] this method has gained a firm place



in synthetic organic chemistry and found widespread use especially in the synthesis of natural products.[15a] A major concern to apply this methodology to the present purpose had been the possibility of two cyclization pathways, 5-*exo-trig* and 6-*endo-trig*. We anticipated, however, that the former would be the favorable pathway, since vinyl radicals are known to be nucleophilic[15a] and the electron density of the anomeric position in **10-13** can be assumed to be comparatively lower than that of the C-2′ position. It is also well-known that radical cyclizations leading to five-membered ring formations are faster than those forming six-membered rings.[15a,b]

As shown in Scheme 2, when a mixture of Bu_3SnH (2

Scheme 2



equiv) and AIBN in benzene was added into a refluxing benzene solution of **10** over 2 h by a syringe pump, a mixture of three products (**14a**, **15a**, and **16**) was obtained after silica gel column chromatography. Separation of these products was accomplished by HPLC. From the ^1H NMR spectra of **14a** and **15a**, it revealed that both products were devoid of an anomeric proton. This observation combined with the presence of two double-doublets (H-2′α and H-2′β) at higher field of around δ 2.3−3.1 ppm suggested their anomeric spiro structures. The yields of **14a** and **15a** were 34.8 and 6.0%, respectively. In contrast to this, the ^1H NMR spectrum of **16** gave a doublet assignable to H-1′ (δ 6.44 ppm, $J_{1',2'}$ = 5.1 Hz). This product was, therefore, assumed to have resulted from 6-*endo* cyclization (the yield of **16**, 7.0%), although its stereochemistry about the 1′- and 2′-positions is not clear at the present time. In order to suppress the thermodynamically favored 6-*endo* cyclization process,[16] photochemically induced radical reaction of **10** at room temperature, $(Bu_3Sn)_2/h\nu$/benzene, was also examined by varying the

(10) ^1H NMR and FAB-MS data of **9** are as follows: ^1H NMR ($CDCl_3$) δ 0.09, 0.10 and 0.11 (12H, each as s), 0.89 and 0.90 (18H, each as s), 3.76 (1H, dd, $J_{4',5'}$ = 5.3, J_{gem} = 11.0 Hz), 3.80 (1H, dd, $J_{4',5'}$ = 4.4 Hz), 4.47 (1H, m), 5.11 (1H, t, $J_{2',3'} = J_{3',4'}$ = 2.8 Hz), 5.33 (1H, d), 6.27 (1H, s), 8.29 (1H, br), 9.75 (1H, s); FAB-MS m/z 483 ($M^+ + H$), 425 ($M^+ -$ Bu-*t*).

(11) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769−3772.

(12) When the reaction between **9** and $Ph_3PC(Br)COPh$ was carried out in DMF at room temperature, partial deformylation occurred to give **7** (13.8%) with a 48.4% recovery of **9**.

(13) *Strukturaufklärung organischer Verbindungen*; Fresenius, W., Huber, J. F. K., Pungor, E., Simon, W., and West, Th. S., Eds.; Springer-Verlag: Berlin, 1986; H215−H220.

(14) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321−2323.

(15) (a) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237−1286. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925−3941.

amount of Bu_3SnH (1–2 equiv). However, no improvement was seen either in terms of the total yield of the cyclized products (**14a**, **15a**, and **16**) or the ratio of 5-*exo*/6-*endo* cyclization.

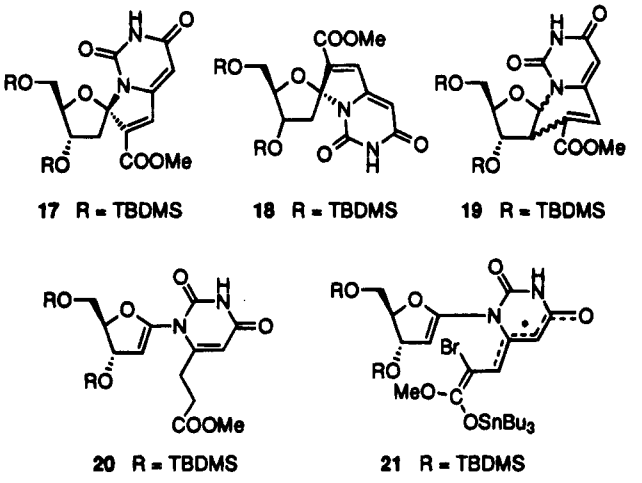
Upon treatment of **14a** and **15a** with Bu_4NF in THF, the corresponding free nucleosides **14b** and **15b** were obtained in crystalline forms and X-ray crystallographic analyses[16b] gave confirmation of their anomeric stereochemistry. The observed preferential formation of the spiro β-nucleoside **14a** may be explicable in terms of steric hindrance: there will be a considerable repulsive force at work when the β-face of the 1-enofuranosyl moiety accommodates the C-6 side chain that carries a vinyl radical, due to the presence of the 4′-β-substituent (CH_2-OTBDMS in this particular case).

It is known that vinyl radicals are configurationally unstable and thus readily isomerize between (*E*)- and (*Z*)-isomers under usual reaction conditions,[17] which certainly offers an advantage from the view point of their cyclization.[14,18] However, when **11**, which has the (*E*)-stereochemistry, was subjected to the AIBN-initiated reaction conditions similar to those employed for **10**, no cyclized product was formed and, quite unexpectedly, a 65% yield of the starting material **11** was recovered intact. We, therefore, then moved to examining the cyclization of **12** and **13** to see whether the difference in the olefinic configuration causes any change in their reaction pathways.

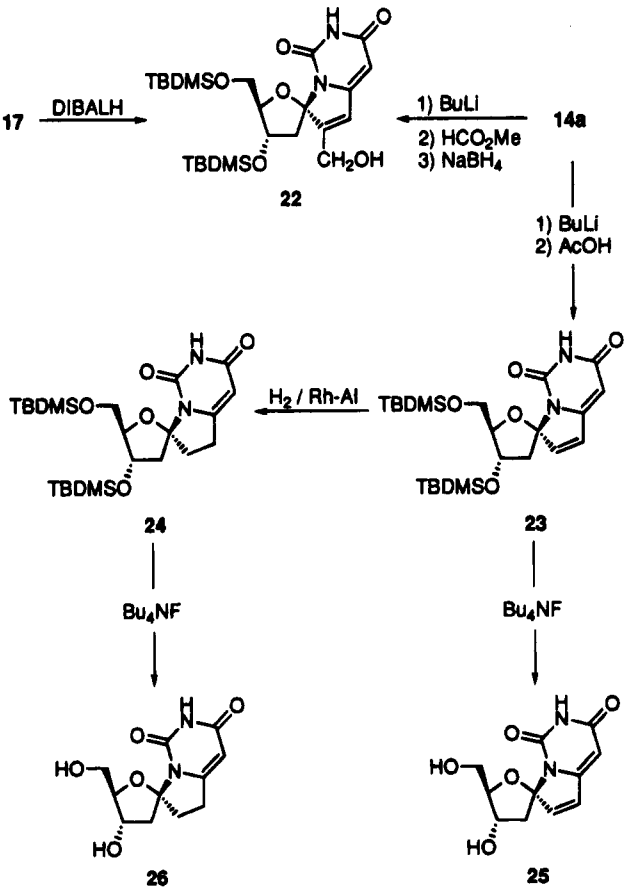
The (*Z*)-isomer **12**, the configuration of which is suitable for the cyclization, gave the products **17** (12.0%), **18** (2.1%), and **19** (6.4%) after reaction with Bu_3SnH (3.5 equiv, over 7 h by a syringe pump) in refluxing benzene followed by HPLC separation. The anomeric stereochemistry of **17** and **18** was confirmed as described in the next section of this text. On the other hand, under exactly the same conditions, the (*E*)-isomer **13** furnished the reduced product **20** (6.1%) along with **17** (6.7%), **18** (2.6%), and **19** (5.0%). Another interesting result from the reaction of **13** is that, when a lesser amount (1 equiv) of Bu_3SnH was used, formation of the (*Z*)-isomer **12** (47.6%) became an observable event.

The above-mentioned experimental results may suggest that, in the presence of a tributyltin radical, **12** and **13** exist as an equilibrium mixture through a highly delocalized radical species depicted as **21** and that the cyclization process occurs preferentially, if not exclusively, from **12**.

Transformations of the Cyclized Products 14a and 17. The dominant formation of **17** over **18** was always the case in the above radical cyclizations of both **12** and **13**. We assumed, therefore, the major isomer **17** would have the 1′-β-configuration. To confirm this point by NOE study, **17** was transformed into the 8-hydroxymethyl derivative **22** by treatment with DIBALH (3 equiv) in Et_2O at 0 °C. However, the NOESY spectrum of **22** gave no enhancement correlation between the methylene protons of the C-8 substituent and H-2′α. Since the β-stereochemistry of **14a** had already become apparent, its conversion to **22** should provide an alternative way of proving the anomeric stereochemistry of **17**. Thus, **14a** was subjected to halogen–lithium exchange by using BuLi (2 equiv) in THF at −78 °C and then the resulting 8-lithio intermediate was treated with HCO_2Me (10 equiv). After extractive workup, the reaction mixture was further treated with $NaBH_4$ in MeOH. This gave **22** (6.1% yield from **14a**, not optimized), the ^1H NMR spectrum of which was identical to the compound prepared from **17**.



Scheme 3



Transformation of **14a** to the 2′-deoxy-6,1′-etheno **23** and 2′-deoxy-6,1′-ethano **24** derivatives was also carried out. Treatment of **14a** with BuLi in THF, followed by quenching with AcOH, gave **23** in 52.4% yield with a 27.6% recovery of **14a**. Selective hydrogenation of the 7,8-double

(16) (a) For a recent example: Satoh, S.; Sodeoka, M.; Sasai, H.; Shibasaki, M. *J. Org. Chem.* **1991**, *56*, 2278–2280. (b) The author has deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(17) Jenkins, P. R.; Symons, M. C. R.; Booth, S. E.; Swain, C. J. *Tetrahedron Lett.* **1992**, *33*, 3543–3546.

(18) (a) Curran, D. P.; Kuo, S.-C. *J. Am. Chem. Soc.* **1986**, *108*, 1106–1107. (b) *Idem. Tetrahedron* **1987**, *43*, 5653–5661. (c) Meyers, A. I.; Lefker, B. A. *Ibid.* **1987**, *43*, 5663–5676.

bond in **23** was accomplished in MeOH with 5% Rh–Al as a catalyst to provide **24** in 86.5% yield. By applying this reduction procedure, it was also possible to convert **14a** directly to **24** in 94.8% yield, although the presence of Et_3N was necessary in this case to avoid partial desilylation.

Finally, deprotection of **23** and **24** was carried out in the conventional way (Bu_4NF in THF), which furnished the corresponding free nucleosides **25** (83.3%) and **26** (93.7%), respectively.

In conclusion, the present study has disclosed a new and straightforward route to the synthesis of anomeric spiro 2'-deoxyuridines. The chemistry involved in this study, lithiation and subsequent radical cyclization, would be applicable to purine nucleosides and, presumably, to other types of glycosides. We are currently investigating along this line.

Experimental Section

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H-NMR spectra were measured at 23 °C (internal standard, Me_4Si) with a JEOL JNM-GX 400 spectrometer. Mass spectra (MS) were taken on a JEOL SX-102A spectrometer in FAB mode (*m*-nitrobenzyl alcohol as a matrix). Ultraviolet spectra (UV) were recorded on a JASCO Ubest-55 spectrophotometer. A commercially available hexane solution of BuLi was titrated before use with diphenylacetic acid in THF.[19] THF was distilled from benzophenone ketyl. Column chromatography was carried out on silica gel (Silica Gel 60, Merck). Thin-layer chromatography (TLC), including preparative TLC, was performed on silica gel (precoated silica gel plate F_{254}, Merck). HPLC was carried out on a Shimadzu LC-6AD with a Shim-pack PREP-SIL (H)·KIT column (2 × 25 cm).

Preparation of 6-Bromovinyl Derivatives 10–13 of 1-[3,5-Bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*erythro*-pent-1-enofuranosyl]uracil. A typical procedure is given below for the preparation of **10**. To a THF (30 mL) solution of LDA (13.2 mmol) was added **5**[9b] (2.00 g, 4.40 mmol) in THF (30 mL) dropwise *via* a syringe while maintaining the temperature below −73 °C. After stirring for 15 min, HCO_2Me (2.98 mL, 48.4 mmol) was added and the reaction mixture was stirred for 0.5 h at −78 °C. The reaction mixture was treated with AcOH (2.52 mL), diluted with EtOAc (20 mL), and evaporated to *ca.* 15 mL. The resulting solution was partitioned between EtOAc and saturated aqueous $NaHCO_3$. The organic layer was separated, dried (Na_2SO_4), and partially purified by short column chromatography on silica gel (EtOAc). This gave crude **9** (2.08 g) as a pale yellow foam, which was used for the Wittig reaction without further purification. Compound **9** in DMF (52 mL) was added at 0 °C to a solution of Ph_3PCBr_2 in CH_2Cl_2, prepared according to the published procedure[11] [Zn powder (575 mg, 8.80 mmol)/Ph_3P (2.31 g, 8.80 mmol)/CBr_4 (2.92 g, 8.80 mmol)/CH_2Cl_2 (27 mL), overnight at room temperature], and the mixture was stirred for 2 h at room temperature. The reaction mixture was diluted with EtOAc (300 mL) and washed successively with 0.2 N aqueous $Na_2S_2O_3$, H_2O, and then brine (50 mL each). The organic layer was dried (Na_2SO_4), evaporated to dryness, and chromatographed on a silica gel column (17–25% EtOAc in hexane). This gave **10** (1.53 g, 54.3% from **5**) as a pale yellow foam.

6-(2,2-Dibromovinyl)-1-[3,5-bis-*O*-(*tert*-Butyldimethylsilyl)-2-deoxy-D-*erythro*-pent-1-enofuranosyl)uracil (10): UV (MeOH) λ_{max} 276 nm (ϵ 9100), λ_{min} 251 nm (ϵ 7800); ^{1}H NMR ($CDCl_3$) δ 0.09 and 0.10 (12H, each as s), 0.90 and 0.91 (18H, each as s), 3.59 (1H, dd, $J_{4',5'}$ = 7.7, J_{gem} = 10.6 Hz), 3.80 (1H, dd, $J_{4',5'}$ = 5.9 Hz), 4.56 (1H, ddd, $J_{3',4'}$ = 2.2 Hz), 4.96 (1H, dd, $J_{2',3'}$=2.6 Hz), 5.19 (1H, d), 6.03 (1H, d, J = 1.1 Hz), 7.11 (1H, d, J = 1.1 Hz), 8.23 (1H, br); FAB-MS *m/z* 641, 639 and 637 (M^+ + H), 625, 623 and 621 (M^+ − Me), 583, 581 and 579 (M^+ − Bu-*t*). Anal. Calcd for $C_{23}H_{38}Br_2N_2O_5Si_2$: C, 43.26; H, 6.00; N, 4.39. Found: C, 43.01; H, 6.19; N, 4.45.

6-(*E*)-(2-Benzoyl-2-bromovinyl)-1-[3,5-bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*erythro*-pent-1-enofuranosyl]-uracil (11). This compound was obtained as a foam in 25.8% yield from **5**: UV (MeOH) λ_{max} 265 nm (ϵ 10800), $\lambda_{shoulder}$ 290 nm (ϵ 7600), λ_{min} 229 nm (ϵ 1200); ^{1}H NMR ($CDCl_3$) δ 0.00, 0.02, and 0.06 (12H, each as s), 0.77 and 0.89 (18H, each as s), 3.57 (1H, dd, $J_{4',5'}$ = 7.1, J_{gem} = 10.6 Hz), 3.75 (1H, dd, $J_{4',5'}$ = 6.2 Hz), 4.38 (1H, ddd, $J_{3',4'}$ = 2.9 Hz), 4.96 (1H, t, $J_{2',3'}$ = 2.9 Hz), 5.25 (1H, d), 6.17 (1H, dd, $J_{5,7}$ = 1.1, $J_{5,NH}$ = 2.2 Hz), 7.18 (1H, d), 7.49–7.53 (2H, m), 7.61–7.65 (1H, m), 7.84–7.87 (2H, m), 8.05 (1H, br); FAB-MS *m/z* 665 and 663 (M^+ + H), 649 and 647 (M^+ − Me), 607 and 605 (M^+ − Bu-*t*), 533 and 531 (M^+ − $OSiMe_2$-Bu-*t*). Anal. Calcd for $C_{30}H_{43}BrN_2O_6Si_2$: C, 54.29; H, 6.53; N, 4.22. Found: C, 53.97; H, 6.68; N, 4.06.

6-(*Z*)-[2-Bromo-2-(methoxycarbonyl)vinyl]-1-[3,5-bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*erythro*-pent-1-enofuranosyl]uracil (12). This compound was obtained as crystals in 35.6% yield from **5**: mp 122–122.5 °C (EtOAc-hexane); UV (MeOH) $\lambda_{shoulder}$ 235 nm (ϵ 9700) and 295 nm (ϵ 6700); ^{1}H NMR ($CDCl_3$) δ 0.05 and 0.08 (12H, each as s), 0.86 and 0.90 (18H, each as s), 3.57 (1H, dd, $J_{4',5'}$ = 8.1, J_{gem} = 10.6 Hz), 3.79 (1H, dd, $J_{4',5'}$ = 6.2 Hz), 3.88 (3H, s), 4.43 (1H, ddd, $J_{3',4'}$ = 2.7 Hz), 4.94 (1H, t, $J_{2',3'}$ = 2.7 Hz), 5.18 (1H, d), 6.13 (1H, t, $J_{5,7}$ = $J_{5,NH}$ = 1.1 Hz), 7.74 (1H, d), 8.37 (1H, br); FAB-MS *m/z* 619 and 617 (M^+ + H), 561 and 559 (M^+ − Bu-*t*), 487 and 485 (M^+ − $OSiMe_2$Bu-*t*). Anal. Calcd for $C_{25}H_{41}BrN_2O_7Si_2$: C, 48.61; H, 6.69; N, 4.54. Found: C, 48.56; H, 6.77; N, 4.56.

6-(*E*)-[2-Bromo-2-(methoxycarbonyl)vinyl]-1-[3,5-bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*erythro*-pent-1-enofuranosyl]uracil (13). This compound was obtained in 14.5% yield from **5** as a solid, which was analytically pure (mp 124.5–125.5 °C): UV (MeOH) $\lambda_{shoulder}$ 241 nm (ϵ 8600) and 275 nm (ϵ 7600); ^{1}H NMR ($CDCl_3$) δ 0.08, 0.085, and 0.09 (12H, each as s), 0.89 and 0.90 (18H, each as s), 3.58 (1H, dd, $J_{4',5'}$ = 7.7, J_{gem} = 10.3 Hz), 3.79 (1H, dd, $J_{4',5'}$ = 6.2 Hz), 3.82 (3H, s), 4.43 (1H, ddd, $J_{3',4'}$ = 2.6 Hz), 4.94 (1H, t, $J_{2',3'}$ = 2.6 Hz), 5.17 (1H, d), 5.64 (1H, dd, $J_{5,7}$ = 1.1, $J_{5,NH}$ = 2.2 Hz), 6.97 (1H, d), 8.31 (1H, br); FAB-MS *m/z* 619 and 617 (M^+ + H), 561 and 559 (M^+ − Bu-*t*), 487 and 485 (M^+ − $OSiMe_2$Bu-*t*). Anal. Calcd for $C_{25}H_{41}BrN_2O_7Si_2 \cdot {}^1/_2H_2O$: C, 47.91; H, 6.76; N, 4.47. Found: C, 48.04; H, 6.83; N, 4.31.

Radical Reaction of the 6-Bromovinyl Derivatives 10–13. A typical procedure is given below for the reaction of **10**. To a refluxing solution of **10** (1.88 g, 2.94 mmol) in benzene (150 mL) was added a mixture of Bu_3SnH (1.58 mL, 5.88 mmol) and AIBN (241 mg, 1.47 mmol) in benzene (20 mL) dropwise over 2 h using a syringe pump. The whole reaction mixture was applied to a silica gel column. Elution with 9–20% EtOAc in hexane gave a mixture of **14a**, **15a**, and **16**. Each product was isolated by HPLC (25% EtOAc in hexane, 10 mL/min) with the following yield and retention time: **14a** (573 mg, 34.8%, 20.9 min); **15a** (99 mg, 6.0%, 22.4 min); **16** (116 mg, 7.0%, 20.0 min).

8-Bromo-3',5'-bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,1'-ethenouridine (14a). This compound was obtained as crystals: mp 179–181 °C (EtOH); UV (MeOH) λ_{max} 296 nm (ϵ 14700), $\lambda_{shoulder}$ 307.5 nm (ϵ 12600), λ_{min} 248 nm (ϵ 7600); ^{1}H NMR ($CDCl_3$) δ 0.05, 0.06, 0.08 and 0.09 (12H, each as s), 0.89 and 0.90 (18H, each as s), 2.46 (1H, dd, $J_{2',3'}$ = 7.7, J_{gem} = 13.9 Hz), 2.78 (1H, dd, $J_{2',3'}$ = 8.1 Hz), 3.88 (2H, d, $J_{4',5'}$ = 5.1 Hz), 4.13 (1H, dt, $J_{3',4'}$ = 7.3 Hz), 4.82 (1H, ddd), 5.62 (1H, d, $J_{5,NH}$ = 2.2 Hz), 6.51 (1H, s), 8.20 (1H, br); FAB-MS *m/z* 561 and 559 (M^+ + H), 545 and 543 (M^+ − Me), 503 and 501 (M^+ − Bu-*t*). Anal. Calcd for $C_{23}H_{39}BrN_2O_5Si_2$: C, 49.36; H, 7.02; N, 5.01. Found: C, 49.50; H, 7.06; N, 4.76.

8-Bromo-3',5'-bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,1'-etheno-α-uridine (15a). This compound was obtained as an oil, which gradually solidified: UV (MeOH) λ_{max} 297 nm (ϵ 15500), $\lambda_{shoulder}$ 286 nm (ϵ 13100), 307.5 nm (ϵ 13400), 324 nm (ϵ 5500), λ_{min} 266 nm (ϵ 8600); ^{1}H NMR ($CDCl_3$) δ 0.06, 0.08 and 0.09 (12H, each as s), 0.90 and 0.91 (18H, each as s), 2.36 (1H, dd, $J_{2'\beta,3'}$ = 8.1, J_{gem} = 12.8 Hz), 3.10 (1H, dd, $J_{2'\alpha,3'}$ = 9.5 Hz), 3.74 (1H, dd, $J_{4',5'}$ = 3.7, J_{gem} = 12.1 Hz), 3.92 (1H, dd, $J_{4',5'}$ =

(19) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–1880.

1.8 Hz), 4.50 (1H, ddd, $J_{3',4'}$ = 8.8 Hz), 4.63 (1H, ddd), 5.62 (1H, d, $J_{5,NH}$ = 2.2 Hz), 6.49 (1H, s), 7.68 (1H, br); FAB-MS *m/z* 561 and 559 ($M^+ + H$), 545 and 543 ($M^+ - Me$), 503 and 501 ($M^+ - Bu\text{-}t$). Anal. Calcd for $C_{23}H_{39}BrN_2O_5Si_2{}^{t}/_2H_2O$: C, 48.58; H, 7.09; N, 4.93. Found: C, 48.70; H, 7.07; N, 4.91.

8-Bromo-3',5'-bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,2'-ethenouridine (16). This compound was obtained as a powder, which was analytically pure: UV (MeOH) λ_{max} 299 nm (ϵ 18200), λ_{min} 253 nm (ϵ 8400); ^{1}H NMR ($CDCl_3$) δ 0.04, 0.15 and 0.17 (12H, each as s), 0.88 and 0.91 (18H, each as s), 3.15 (1H, m), 3.38 (1H, dd, $J_{4',5'}$ = 7.7, J_{gem} = 10.6 Hz), 3.64 (1H, dd, $J_{4',5'}$ = 4.4 Hz), 3.93 (1H, dd), 4.83 (1H, s), 5.54 (1H, br s), 6.44 (1H, d, $J_{1',2'}$ = 5.1 Hz), 6.54 (1H, d, $J_{7,NH}$ = 2.2 Hz), 8.34 (1H, br); FAB-MS *m/z* 561 and 559 ($M^+ + H$), 545 and 543 ($M^+ - Me$), 503 and 501 ($M^+ - Bu\text{-}t$). Anal. Calcd for $C_{23}H_{39}BrN_2O_5Si_2{}^{t}/_4H_2O$: C, 48.97; H, 7.06; N, 4.97. Found: C, 48.94; H, 7.38; N, 4.87.

8-Bromo-2'-deoxy-6,1'-ethenouridine (14b). Compound **14a** (115 mg, 0.21 mmol) was dissolved in THF (5 mL). To this were added AcOH (35 μL, 0.62 mmol) and $Bu_4NF{\cdot}3H_2O$ (162 mg, 0.51 mmol), and the mixture was stirred overnight at room temperature. Evaporation of the solvent followed by silica gel column chromatography (1–5% MeOH in CH_2Cl_2) gave **14b** (57.4 mg, 84.4%) as a solid, which was crystallized from EtOH: mp 205 °C dec; UV (MeOH) λ_{max} 296 nm (ϵ 15200), $\lambda_{shoulder}$ 283.5 nm (ϵ 12700), 306.5 nm (ϵ 13000); ^{1}H NMR (DMSO-d_6) δ 2.27 (1H, dd, $J_{2',3'}$ = 8.4, J_{gem} = 13.9 Hz), 2.80 (1H, dd, $J_{2',3'}$ = 8.4 Hz), 3.54 (1H, ddd, $J_{4',5'}$ = 8.1, $J_{5',OH}$ = 5.5, J_{gem} = 11.7 Hz), 3.64 (1H, ddd, $J_{4',5'}$ = 2.2, $J_{5',OH}$ = 5.5 Hz), 3.91 (1H, dt, $J_{3',4'}$ = 8.1 Hz), 4.57 (1H, ddt, $J_{3',OH}$ = 5.5 Hz), 4.70 (1H, t), 5.42 (1H, d), 5.66 (1H, s), 7.02 (1H, s), 11.12 (1H, br); FAB-MS *m/z* 355 and 353 ($M^+ + Na$), 333 and 331 ($M^+ + H$). Anal. Calcd for $C_{11}H_{11}BrN_2O_5$: C, 39.90; H, 3.35; N, 8.46. Found: C, 40.20; H, 3.18; N, 8.27.

8-Bromo-2'-deoxy-6,1'-etheno-α-uridine (15b). This compound was obtained as a solid in 88.8% yield from **15a** by the procedure described for the preparation of **14b**. Crystallization from EtOH gave an analytically pure sample: mp 233 °C dec; UV (MeOH) λ_{max} 260 nm (ϵ 9100) and 296 nm (ϵ 15600), $\lambda_{shoulder}$ 271 nm (ϵ 13500) and 307 nm (ϵ 14000), λ_{min} 278 nm (ϵ 9000); ^{1}H NMR (DMSO-d_6) δ 2.33 (1H, dd, $J_{2',3'}$ = 8.2, J_{gem} = 13.6 Hz), 2.91 (1H, dd, $J_{2',3'}$ = 9.2 Hz), 3.40 (1H, dd, $J_{4',5'}$ = 7.0, J_{gem} = 12.1 Hz), 3.65 (1H, dd, $J_{4',5'}$ = 2.2 Hz), 4.14 (1H, m), 4.27 (1H, ddd, $J_{3',4'}$ = 8.8 Hz), 4.77 (1H, t, J = 5.5 Hz), 5.48 (1H, d, J = 5.1 Hz), 5.68 and 6.99 (2H, each as s), 11.19 (1H, br); FAB-MS *m/z* 333 and 331 ($M^+ + H$). Anal. Calcd for $C_{11}H_{11}BrN_2O_5$: C, 39.90; H, 3.35; N, 8.46. Found: C, 40.24; H 3.27; N, 8.52.

3',5'-Bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,1'-etheno-8-(methoxycarbonyl)uridine (17). This compound was obtained as crystals in 12.0% yield from **12** after HPLC separation (33% EtOAc in hexane, retention time 16.3 min): mp 209–209.5 °C (EtOAc–hexane); UV (MeOH) λ_{max} 318 nm (ϵ 8800), λ_{min} 278 nm (ϵ 4400); ^{1}H NMR ($CDCl_3$) δ 0.05 and 0.08 (12H, each as s), 0.88 and 0.89 (18H, each as s), 2.72 (1H, dd, $J_{2'\alpha,3'}$ = 8.4, J_{gem} = 13.4 Hz), 2.80 (1H, dd, $J_{2'\beta,3'}$ = 7.9 Hz), 3.87–3.88 (2H, m), 3.90 (3H, s), 4.26 (1H, ddd, $J_{3',4'}$ = 7.9, $J_{4',5'}$ = 7.3, $J_{4',5'}$ = 3.3 Hz), 4.80 (1H, dt), 5.79 (1H, d, $J_{5,NH}$ = 1.8 Hz), 7.06 (1H, s), 8.11 (1H, br); FAB-MS *m/z* 561 ($M^+ + Na$), 539 ($M^+ + H$), 523 ($M^+ - Me$), 481 ($M^+ - Bu\text{-}t$). Anal. Calcd for $C_{25}H_{42}N_2O_7Si_2{}^{t}/_3H_2O$: C, 55.12; H, 7.89; N, 5.14. Found: C, 55.49; H, 7.93; N, 4.76.

3',5'-Bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,1'-etheno-8-(methoxycarbonyl)-α-uridine (18). After HPLC separation (retention time 18.3 min), this compound was obtained in 2.1% yield from **12** as an oil, which gradually solidified: UV (MeOH) λ_{max} 318 nm (ϵ 10500), λ_{min} 280 nm (ϵ 5200); ^{1}H NMR ($CDCl_3$) δ 0.03, 0.05, 0.07 and 0.09 (12H, each as s), 0.88 and 0.90 (18H, each as s), 2.64 (1H, dd, $J_{2'\beta,3'}$ = 8.1, J_{gem} = 12.8 Hz), 3.09 (1H, dd, $J_{2'\alpha,3'}$ = 8.4 Hz), 3.70 (1H, dd, $J_{4',5'}$ = 5.9, J_{gem} = 11.7 Hz), 3.84 (3H, s), 3.87 (1H, dd, $J_{4',5'}$ = 1.8 Hz), 4.58 (1H, ddd, $J_{3',4'}$ = 8.4 Hz), 4.72 (1H, dt), 5.80 (1H, d, $J_{5,NH}$ = 1.8 Hz), 6.98 (1H, s), 7.99 (1H, br); FAB-MS *m/z* 539 ($M^+ + H$), 523 ($M^+ - Me$), 481 ($M^+ - Bu\text{-}t$). Anal. Calcd for $C_{25}H_{42}N_2O_7Si_2$: C, 55.73; H, 7.86; N, 5.20. Found: C, 55.74; H, 7.94; N, 5.06.

3',5'-Bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,2'-etheno-8-(methoxycarbonyl)uridine (19). After HPLC separation (retention time 15.5 min), this compound was obtained in 6.4% yield from **12** as a powder: UV (MeOH) λ_{max} 243 nm (ϵ 9600) and 312 nm (ϵ 14800), λ_{min} 275 nm (ϵ 5400); ^{1}H NMR ($CDCl_3$) δ –0.02, –0.01, 0.13 and 0.18 (12H, each as s), 0.84 and 0.92 (18H, each as s), 3.19 (1H, m), 3.23 (1H, dd, $J_{4',5'}$ = 8.1, J_{gem} = 10.6 Hz), 3.57 (1H, dd, $J_{4',5'}$ = 4.4 Hz), 3.87 (3H, s), 3.88–3.90 (1H, m), 4.71 (1H, s), 5.78 (1H, m), 6.52 (1H, d, $J_{1',2'}$ = 5.1 Hz), 7.04 (1H, d, $J_{5,7}$ = 2.6 Hz), 8.28 (1H, br); FAB-MS *m/z* 539 ($M^+ + H$), 523 ($M^+ - Me$), 481 ($M^+ - Bu\text{-}t$). Anal. Calcd for $C_{25}H_{42}N_2O_7Si_2$: C, 55.73; H, 7.86; N, 5.20. Found: C, 55.40; H, 8.11; N, 5.30.

1-[3,5-Bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*erythro*-pent-1-enofuranosyl]-6-[(2-methoxycarbonyl)ethyl]-uracil (20). This compound was obtained in 6.1% yield from **13** as an oil: UV (MeOH) λ_{max} 258 nm (ϵ 10300) and 317 nm (ϵ 1400), λ_{min} 230 nm (ϵ 4600) and 295 nm (ϵ 1000); ^{1}H NMR ($CDCl_3$) δ 0.08, 0.084, and 0.09 (12H, each as s), 0.88 and 0.90 (18H, each as s), 2.64 and 2.88 (4H, each as t, J = 7.3 Hz), 3.64 (1H, dd, $J_{4',5'}$ = 7.3, J_{gem} = 10.6 Hz), 3.70 (3H, s), 3.80 (1H, dd, $J_{4',5'}$ = 5.9 Hz), 4.46 (1H, ddd, $J_{3',4'}$ = 2.2 Hz), 4.99 (1H, dd, $J_{2',3'}$ = 2.6 Hz), 5.20 (1H, d), 5.59 (1H, d, $J_{5,NH}$ = 2.2 Hz), 8.09 (1H, br); FAB-MS *m/z* 563 ($M^+ + Na$), 541 ($M^+ + H$), 525 ($M^+ - Me$), 483 ($M^+ - Bu\text{-}t$), 409 ($M^+ - OSiMe_2Bu\text{-}t$). Anal. Calcd for $C_{25}H_{44}N_2O_7Si_2H_2O$: C, 53.73; H, 8.30; N, 5.01. Found: C, 53.92; H, 8.09; N, 4.85.

3',5'-Bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-8-(hydroxymethyl)-6,1'-ethenouridine (22). A toluene solution of DIBALH (0.54 mmol) was added to **17** (96.2 mg, 0.18 mmol) in Et_2O (10 mL) at 0 °C. The resulting solution was stirred overnight at the same temperature. After workup of the reaction mixture followed by silica gel column chromatography (17–33% EtOAc in hexane), **22** (47.3 mg, 51.7%) was obtained as an analytically pure powder: UV (MeOH) λ_{max} 290 nm (ϵ 14600), $\lambda_{shoulder}$ 278 nm (ϵ 11800) and 300 nm (ϵ 13100); ^{1}H NMR ($CDCl_3$) δ 0.069, 0.07, 0.13, and 0.14 (12H, each as s), 0.90 and 0.91 (18H, each as s), 2.27 (1H, dd, $J_{2',3'}$ = 3.3, J_{gem} = 14.7 Hz), 3.01 (1H, t, J = 5.5 Hz), 3.34 (1H, dd, $J_{2',3'}$ = 7.3 Hz), 3.78 (1H, dd, $J_{4',5'}$ = 6.2, J_{gem} = 10.8 Hz), 3.98 (1H, dd, $J_{4',5'}$ = 7.0 Hz), 4.13 (1H, ddd, $J_{3',4'}$ = 3.3 Hz), 4.49 and 4.58 (2H, each as dd, J_{gem} = 15.8 Hz), 4.71 (1H, dt), 5.60 (1H, d, $J_{5,NH}$ = 2.2 Hz), 6.28 (1H, d, J = 1.5 Hz), 8.00 (1H, br); FAB-MS *m/z* 511 ($M^+ + H$), 495 ($M^+ - Me$), 453 ($M^+ - Bu\text{-}t$). Anal. Calcd for $C_{24}H_{42}N_2O_6Si_2{}^{t}/_2H_2O$: C, 55.46; H, 8.34; N, 5.39. Found: C, 55.44; H, 8.29; N, 5.23.

3',5'-Bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,1'-ethenouridine (23). Compound **14a** (79.1 mg, 0.14 mmol) was dissolved in THF (5 mL) and treated with a hexane solution of BuLi (0.21 mmol) at below –75 °C. The reaction mixture was stirred for 0.5 h and quenched with AcOH. After extractive workup, the mixture was purified by preparative TLC (33% EtOAc in hexane). This gave **23** (35.5 mg, 52.4%) as a solid along with the recovered **14a** (21.8 mg, 27.6%). Crystallization of **23** from EtOAc–hexane gave an analytical sample (mp 272–272.5 °C): UV (MeOH) λ_{max} 291 nm (ϵ 13000), $\lambda_{shoulder}$ 302.5 nm (ϵ 11200), λ_{min} 245 nm (ϵ 5100); ^{1}H NMR ($CDCl_3$) δ 0.06, 0.07, 0.10, and 0.12 (12H, each as s), 0.90 and 0.91 (18H, each as s), 1.99 (1H, dd, $J_{2'\alpha,3'}$ = 2.2, J_{gem} = 13.6 Hz), 3.35 (1H, dd, $J_{2'\beta,3'}$ = 5.3 Hz), 3.72 (1H, dd, $J_{4',5'}$ = 5.5, J_{gem} = 10.6 Hz), 3.86 (1H, dd, $J_{4',5'}$ = 8.8 Hz), 4.07 (1H, ddd, $J_{3',4'}$ = 1.8 Hz), 4.62 (1H, ddd), 5.64 (1H, d, $J_{5,NH}$ = 2.2 Hz), 6.28 and 6.82 (2H, each as d, $J_{7,8}$ = 5.9 Hz), 8.03 (1H, br); FAB-MS *m/z* 503 ($M^+ + Na$), 481 ($M^+ + H$), 465 ($M^+ - Me$), 423 ($M^+ - Bu\text{-}t$). Anal. Calcd for $C_{23}H_{40}N_2O_5Si_2$: C, 57.46; H, 8.39; N, 5.83. Found: C, 57.68; H, 8.71; N, 5.76.

3',5'-Bis-*O*-(*tert*-butyldimethylsilyl)-2'-deoxy-6,1'-ethanouridine (24). A mixture of **14a** (74.0 mg, 0.13 mmol), Et_3N (18.4 μL, 0.13 mmol), and 5% Rh–Al (22 mg) in MeOH (10 mL) was hydrogenated with stirring overnight at room temperature. Purification of the mixture by silica gel column chromatography (33% EtOAc in hexane) gave **24** (60.4 mg, 94.8%) as a solid, which was crystallized from Et_2O–hexane (mp 177–178 °C): UV (MeOH) λ_{max} 261 nm (ϵ 12500), λ_{min} 235 nm (ϵ 5000); ^{1}H NMR ($CDCl_3$) δ 0.037, 0.04, 0.08, and 0.09 (12H, each as s), 0.88 and 0.90 (18H, each as s), 1.99 (1H, dd, $J_{2',3'}$ = 4.8, J_{gem} = 13.6 Hz), 2.16 (1H, ddd, $J_{7,8}$ = 8.4 and 11.0, J_{gem} = 13.2 Hz), 2.45

(1H, ddd, $J_{7,8}$ = 1.5 and 8.1 Hz), 2.76 (1H, dd, J_{gem} = 16.9 Hz), 3.02 (1H, m), 3.42 (1H, dd, $J_{2',3'}$ = 6.6 Hz), 3.66 (1H, dd, $J_{4',5'}$ = 5.9, J_{gem} = 11.0 Hz), 3.77 (1H, dd, $J_{4',5'}$ = 5.9 Hz), 3.84 (1H, dt, $J_{3',4'}$ = 5.5 Hz), 4.60 (1H, ddd), 5.53 (1H, br), 8.06 (1H, br); FAB-MS *m/z* 505 (M^+ + Na), 483 (M^+ + H), 467 (M^+ − Me), 425 (M^+ − Bu-*t*). Anal. Calcd for $C_{23}H_{42}N_2O_5Si_2$: C, 57.22; H, 8.77; N, 5.80. Found: C, 56.96; H, 8.82; N, 5.87.

2'-Deoxy-6,1'-ethenouridine (25). This compound was obtained as a solid in 83.3% yield from **23** by the procedure described for the preparation of **14b** from **14a**. Crystallization from EtOH gave an analytical sample (mp 192−192.5 °C): UV (MeOH) λ_{max} 290 nm (ϵ 12400), $\lambda_{shoulder}$ 299 nm (ϵ 10800), λ_{min} 246 nm (ϵ 4000); ^{1}H NMR (DMSO-d_6) δ 2.07 (1H, dd, $J_{2',3'}$ = 4.4, J_{gem} = 13.9 Hz), 2.97 (1H, dd, $J_{2',3'}$ = 6.6 Hz), 3.50 (1H, ddd, $J_{5',OH}$ = 5.5, $J_{4',5'}$ = 6.0, J_{gem} = 11.9 Hz), 3.62 (1H, ddd, $J_{5',OH}$ = 5.5, $J_{4',5'}$ = 4.4 Hz), 3.89 (1H, dt, $J_{3',4'}$ = 4.4 Hz), 4.46 (1H, m), 4.69 (1H, t), 5.35 (1H, d, $J_{3',OH}$ = 4.0 Hz), 5.67 (1H, d, $J_{5,NH}$ = 1.8 Hz), 6.56 (1H, d, $J_{7,8}$ = 5.9 Hz), 6.66 (1H, d), 11.05 (1H, br); FAB-MS *m/z* 253 (M^+ + H). Anal. Calcd for $C_{11}H_{12}N_2O_5 \cdot {}^1/_3H_2O$: C, 51.17; H, 4.94; N, 10.85. Found: C, 50.93; H, 5.21;N, 10.48.

2'-Deoxy-6,1'-ethanouridine (26). This compound was obtained as a hygroscopic powder in 93.7% yield from **24** by the procedure described for the preparation of **14b** from **14a**: UV (MeOH) λ_{max} 261 nm (ϵ 10600), λ_{min} 230 nm (ϵ 2200); ^{1}H NMR (DMSO-d_6) δ 1.98 (1H, dd, $J_{2',3'}$ = 5.9, J_{gem} = 13.6 Hz), 2.14−2.28 (2H, m), 2.75−2.89 (2H, m), 3.11 (1H, dd, $J_{2',3'}$ = 7.7 Hz), 3.37 (1H, dd, $J_{4',5'}$ = 6.6, J_{gem} = 11.7 Hz), 3.56 (1H, dd, $J_{4',5'}$ = 3.7 Hz), 3.67 (1H, ddd, $J_{3',4'}$ = 5.9 Hz), 4.32 (1H, ddd), 4.65 (1H, t, $J_{5',OH}$ = 5.9 Hz), 5.14 (1H, d, $J_{3',OH}$ = 4.8 Hz), 5.47 (1H, d, $J_{5,NH}$ = 1.8 Hz), 11.0 (1H, br); FAB-MS *m/z* 255 (M^+ + H). Anal. Calcd for $C_{11}H_{14}N_2O_5 \cdot {}^4/_5H_2O$: C, 49.18; H, 5.85; N, 10.43. Found: C, 49.13; H, 5.66; N, 10.08.

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