Synthesis of 2′,3′-Didehydro-2′,3′-dideoxynucleosides by Reaction of 5′-Protected Nucleoside 2′,3′-Dimesylates with Telluride Dianion: A General Route from *Cis* Vicinal Diols to Olefins

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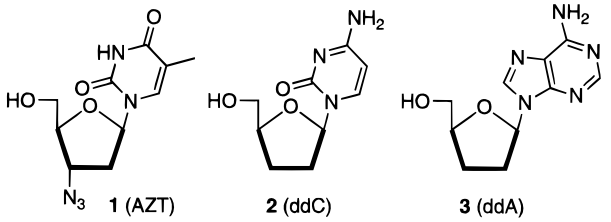
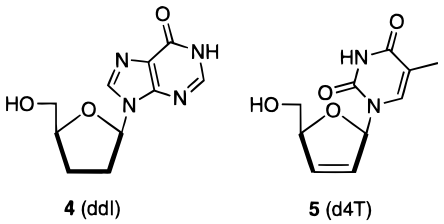
2′,3′-Dimesylates of 5′-protected nucleosides are converted into the corresponding 2′,3′-didehydro-2′,3′-dideoxy compounds by treatment with telluride dianion in the form of the sodium or lithium salt. The method is well-suited to the preparation of unsaturated nucleosides that can be converted into compounds that are believed to be useful in the treatment of AIDS. The deoxygenation is general for vicinal dimesylates that have, or may adopt, a synperiplanar conformation. With straight chain compounds the reaction is stereospecific. In some cases, similar, but slower, deoxygenations can be performed with selenide dianion.

Introduction

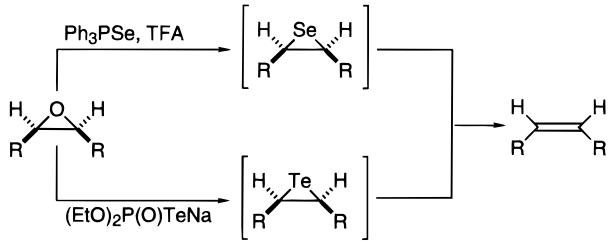
Replication of the human immunodeficiency virus is disrupted by certain deoxy nucleosides,[1] and several compounds of this type are currently important because of their potential, or actual, merit in the treatment of AIDS. The best known of these compounds[2] are 3′-azido-3′-deoxythymidine (**1**, AZT), 2′,3′-dideoxycytidine (ddC, **2**), 2′,3′-dideoxyadenosine (ddA, **3**), 2′,3′-dideoxyinosine (ddI, **4**), and 2′,3′-didehydro-3′-deoxythymidine (d4T, **5**), and the development of synthetic routes to these, and related, materials has become a prominent subject[3,4] in medicinal chemistry.





2′,3′-Dideoxynucleosides are often made from suitably protected nucleosides, and at least two approaches are used: (a) replacement of hydroxyl groups by hydrogen),[5] and (b) double deoxygenation to the 2′,3′-didehydro-2′,3′-dideoxy compound, followed by hydrogenation. Both routes have been examined extensively,[3,6−8] but the development of new methodology is warranted[9] in view of the medical and commercial importance of the area. We report full details[10] of an approach based on tellurium chemistry.

Scheme 1



The starting point for this work was our experience in converting epoxides into olefins by treatment with triphenylphosphine selenide in the presence of acid (Scheme 1)[11] or by treatment with sodium diethyl phosphorotel-

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

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(2) (a) FDA approval has been granted for AZT, DDC, DDI, and D4T: *Chem. Eng. News* **1994**, *72*(27), 22 (July 4, 1994). (b) DDI is made from DDA by enzymatic replacement of the NH_2 by OH: Beach, C. M.; Evans, R. K.; Coleman, M. S. *Nucleosides Nucleotides* **1991**, *10*, 1499.

(3) For a review on AIDS-driven nucleoside chemistry: Huryn, D. M.; Okabe, M. *Chem. Rev.* **1992**, *92*, 1745.

(4) Dueholm, K. L.; Pedersen, E. B. *Synthesis* **1992**, 1.

(5) In the case of the thymidine series, only 3′-deoxygenation would, of course, be needed.

(6) (a) Block, E. *Org. React. (N.Y.)* **1984**, *30*, 457. (b) Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989; p 155.

(7) For more recent developments, see: (a) Liu, Z.; Classon, B.; Samuelsson, B. *J. Org. Chem.* **1990**, *55*, 4273 and references therein. (b) Luzzio, F. A.; Menes, M. E. *J. Org. Chem.* **1994**, *59*, 7267.

(8) For recent examples of the preparation of 2′,3′-dideoxynucleosides from nucleosides, see: (a) Dunkel, M.; Pfleiderer, W. *Nucleosides Nucleotides* **1992**, *11*, 787. (b) Seela, F.; Muth, H.-P.; Bindig, U. *Synthesis* **1988**, 670. (c) Robins, M. J.; Hansske, F.; Low, N. H.; Park, J. I. *Tetrahedron Lett.* **1984**, *25*, 367. (d) Talekar, R. R.; Coe, P. L.; Walker, R. T. *Synthesis* **1993**, 303, and references therein. (e) Nair, V. *Nucleosides Nucleotides* **1989**, *8*, 699. (f) Prisbe, E. J.; Martin, J. C. *Synth. Commun.* **1985**, *15*, 401. (g) Lin, T.-S.; Yang, J.-H.; Liu, M.-C.; Zhu, J.-L. *Tetrahedron Lett.* **1990**, *31*, 3829. (h) Yamaguchi, T.; Saneyoshi, M. *Nucleosides Nucleotides* **1992**, *11*, 373. (i) Dorland, E.; Serafinowski, P. *Synthesis* **1992**, 477. (j) Chu, C. K.; Bhadti, V. S.; Doboszewski, B.; Gu, Z. P.; Kosugi, Y.; Pullaiah, K. C.; Van Roey, P. *J. Org. Chem.* **1989**, *54*, 2217. (k) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1991**, *32*, 7187. (l) Chen, B.-C.; Quinlan, S. L.; Stark, D. R.; Reid, J. G.; Audia, V. H.; George, J. G.; Eisenreich, E.; Brundidge, S. P.; Racha, S.; Spector, R. H. *Tetrahedron Lett.* **1995**, *36*, 7957.

(9) For an evaluation of some of the classical methods, see: (a) References 8j. (b) Mansuri, M. M.; Starrett, J. E., Jr.; Wos, J. A.; Tortolani, D. R.; Brodfuehrer, P. R.; Howell, H. G.; Martin, J. C. *J. Org. Chem.* **1989**, *54*, 4780.

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(11) Clive, D. L. J.; Denyer, C. V. *J. Chem. Soc., Chem. Commun.* **1973**, 253.

(12) Clive, D. L. J.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2347.

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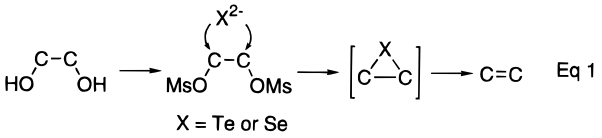
luroate (Scheme 1).[12] In each case, we interpreted the course of the reaction in terms of a three-membered ring intermediate, which spontaneously expelled the heavy atom.[13,14] With this as background, we wondered if vicinal dimesylates might also be converted, transiently, into epitellurides or episelenides and then into olefins by the action of Na_2Te or Na_2Se, respectively (eq 1).



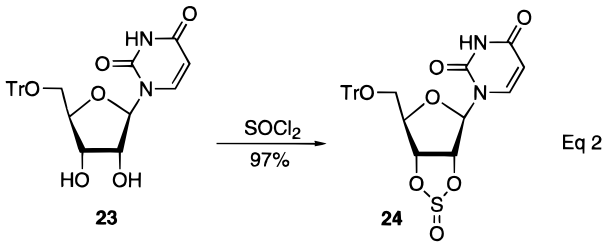
Eq 1

Vicinal dibromides have been converted into olefins by reaction with telluride[15] or selenide[16] dianions, but the use of dimesylates would be more readily applicable to ribonucleosides by direct esterification of the hydroxyl groups. In the event, the reaction summarized by eq 1 was easily reduced to practice, especially for X = Te, and our results are collected in Table 1; the method is mild, efficient, and general. We examined first the naphthalene derivative **6** (Table 1, entry 1), and then we made a survey of the main variables.

Use of Dimesylates. Our procedure requires that each of the vicinal hydroxyl groups be converted into a leaving group of such a type that only the original hydroxyl-bearing carbon—and not the other oxygen attachment—be susceptible to nucleophilic attack. This requirement is normally satisfied by sulfonate esters, and from the outset, we used dimesylates, which are simple and cheap to prepare.[17] Yields in our mesylations were generally above 80%.

In one case (Table 1, entry 12) we also examined a ditosylate, but could detect no advantage, and in fact, the yield was lower in both steps than for the corresponding dimesylate.

Cyclic sulfates were also considered,[18,19] but we found these compounds difficult to make (by oxidation of the corresponding sulfites)—at least in the few examples that we tried.[20] Cyclic sulfites,[21] in contrast, are easy to prepare (e.g., eq 2) but, at least with **24** as a test case, those do not give olefins under our standard conditions, the starting diol being recovered.[19b,22]



Eq 2

Simple vicinal dimesylates have been converted into olefins by the action of sodium naphthalenide[23] or of iodide ion,[24] and so we tested both of these systems on the dimesylate **9**. With sodium naphthalenide, a complex mixture resulted, and with NaI/18-crown-6/Zn dust or NaI/18-crown-6/Zn−Cu couple (in DMF) we did not detect formation of the olefin.

Source of Telluride Dianion. Many of our experiments were carried out on a small scale, and for reasons of convenience we generated the telluride dianion by addition of Et_3BHLi (Super-Hydride) to metallic Te.[25] The Et_3B liberated in these reactions does not seem to play a significant part[13] in the deoxygenation, because the same results are obtained by generating the telluride dianion from Na and Te in liquid NH_3—a process, of course, that affords reagent free of Lewis acids.

We also evaluated several other known, and potential, ways of generating the telluride dianion, and some of these are listed in Table 2. Apart from the Te/Et_3BHLi and Na/Te/liquid NH_3 systems of Table 1 and Te/*s*-Bu_3-BHLi (Table 2), none of the methods was successful, and in many cases we formed the impression that the presence of base led to destruction of the starting material and/or product.

In the small-scale experiments summarized in Table 2, we sometimes found that an excess of reducing agent was needed to dissolve all the Te, and in these cases we often obtained a poor yield. For this reason, we sought to quench any excess of hydride (in an experiment with Et_3BHLi) by addition of acetone (Table 2, entry 11) or of EtOH (Table 2, entry 12), but any potential advantage was offset by the (deleterious) generation of alkoxide.

In our hands, several of the reported preparations of telluride dianion gave material that was probably con-

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(14) Recent reviews on the use of tellurium reagents: (a) Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 793. (b) Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 897. (c) Petragnani, N. *Tellurium in Organic Synthesis*; Academic Press: London, 1994.

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(16) Prince, M.; Bremer, B. W.; Brenner, W. *J. Org. Chem.* **1966**, *31*, 4292.

(17) (a) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; p 662. (b) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

(18) *Cf.* Beels, C. M. D.; Coleman, M. J.; Taylor, R. J. K. *Synlett* **1990**, 479.

(19) (a) Berridge, M. S.; Franceschini, M. P.; Rosenfeld, E.; Tewson, T. J. *J. Org. Chem.* **1990**, *55*, 1211. (b) Tewson, T. J. *J. Org. Chem.* **1983**, *48*, 3507. (c) Tewson, T. J.; Soderlind, M. *J. Carbohydr. Chem.* **1985**, *4*, 529. (d) Lowe, G.; Salamone, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1392. (e) Chai, C. L. L.; Hepburn, T. W.; Lowe, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1403. (f) Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538. (g) Kim, B. M.; Sharpless, K. B. *Tetrahedron Lett.* **1989**, *30*, 655.

(20) Reaction of cyclic sulfates with Te^{2-} has been reported recently for preparation of alkenes in the sugar series: Chao, B.; McNulty, K. C.; Dittmer, D. C. *Tetrahedron Lett.* **1995**, *36*, 7209.

(21) *Cf.* Gao, Y.; Zepp, C. M. *Tetrahedron Lett.* **1991**, *32*, 3155 and references therein.

(22) *Cf.* Carlsen, P. H. J.; Aase, K. *Acta Chem. Scand.* **1993**, *47*, 617.

(23) (a) Carnahan, J. C., Jr.; Closson, W. D. *Tetrahedron Lett.* **1972**, 3447. (b) *Cf.* Guijarro, D.; Mancheño, B.; Yus, M. *Tetrahedron Lett.* **1992**, *33*, 5597.

(24) E.g. (a) Bladon, P.; Owen, L. N. *J. Chem. Soc.* **1950**, 598. (b) Wendler, N. L.; Slates, H. L.; Tischler, M. *J. Am. Chem. Soc.* **1952**, *74*, 4894. (c) Köll, P.; Kopf, J.; Metzger, J. O.; Schwarting, W.; Oelting, M. *Liebigs Ann. Chem.* **1987**, 199. (d) Baptistella, L. H. B.; Neto, A. Z.; Onaga, H.; Godoi, E. A. M. *Tetrahedron Lett.* **1993**, *34*, 8407. (e) Anzai, K.; Matsui, M. *Agric. Biol. Chem.* **1973**, *37*, 345. (f) Yadav, J. S.; Sreenivasa Rao, E.; Sreenivasa Rao, V. *Synth. Commun.* **1989**, *19*, 705. (g) *Cf.* Cleophax, J.; Hildesheim, J.; Gero, S. D. *Bull. Soc. Chim. Fr.* **1967**, 4111.

(25) Clive, D. L. J.; Anderson, P. C.; Moss, N.; Singh, A. *J. Org. Chem.* **1982**, *47*, 1641, and references therein.

(26) Björgvinsson, M.; Schrobilgen, G. J. *Inorg. Chem.* **1991**, *30*, 2540.

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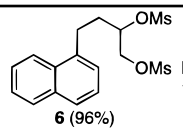
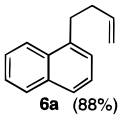
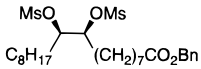
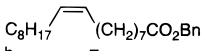
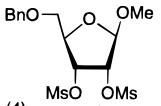
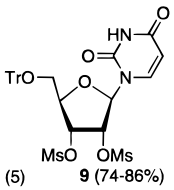
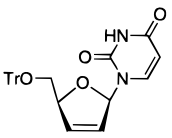
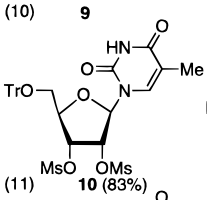
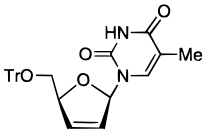
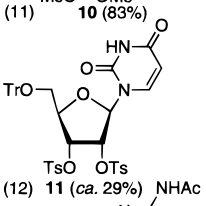
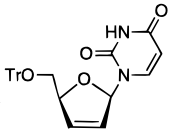
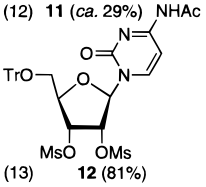
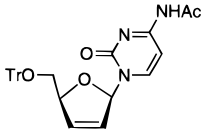
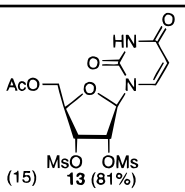
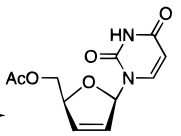
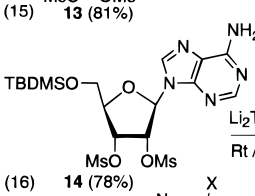
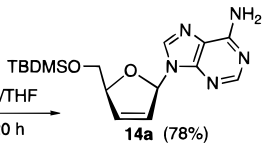
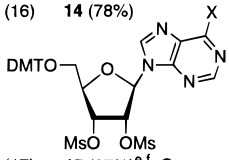
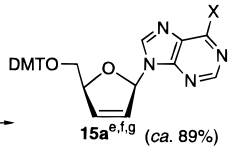
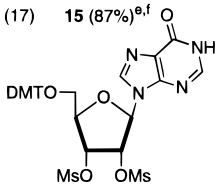
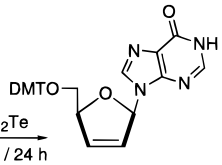
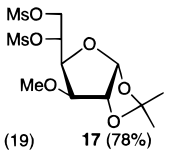
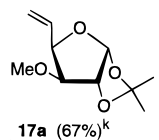
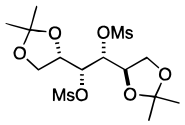
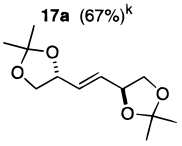
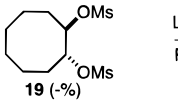
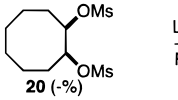
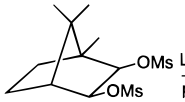
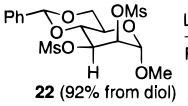
(28) (a) Higa, K. T.; Harris, D. C. *Organometallics* **1989**, *8*, 1674. (b) Junk, T.; Gritzner, G.; Irgolic, K. J. *Synth. React. Inorg. Met.-Org. Chem.* **1989**, *19*, 931. (c) Tschugaeff, L.; Choplin, W. *Chem. Ber.* **1914**, *47*, 1269. (d) Spencer, H. K.; Cava, M. P. *J. Org. Chem.* **1977**, *42*, 2937. (e) Lue, P.; Chen, B.; Yu, X.; Chen, J.; Zhou, X. *Synth. Commun.* **1986**, *16*, 1849. (f) *Cf.* Bergman, J.; Engman, L. *Z. Naturforsch. B* **1980**, *35*, 217. (g) *Cf.* Lalancette, J. M.; Arnac, M. *Can. J. Chem.* **1969**, *47*, 3695. (h) Chen, J.; Zhou, X. J. *Synthesis* **1987**, 586. (i) Suzuki, H.; Inouye, M. *Chem. Lett.* **1986**, 403. (j) Suzuki, H.; Manabe, H.; Kawaguchi, T.; Inouye, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 771. (k) Suzuki, H.; Nakamura, T. *J. Org. Chem.* **1993**, *58*, 241.

Table 1[a]

	Dimesylate (Yield from diol)		Olefin
(1)	 **6** (96%)	Li_2Te/THF, Rt / 20 h	 **6a** (88%)
(2)	 **7** (*ca.* 95%)	Li_2Te/THF, Rt / 14 h, Bath 100 °C / 2 h	 **7a** (83%)
(3)	**7**	Li_2Se/THF-Dioxane, Rt 24 h, Bath 100 °C / 4 h	**7a** (76%)
(4)	 **8** (93%)	Li_2Te/THF-Dioxane, Bath 105 °C / 20 h	 **8a** (69%)
(5)	 **9** (74-86%)	Na_2Te/THF, Rt / 20 h	 **9a** (75-93%)
(6)	**9**	Li_2Te/THF-Dioxane, Rt / 48 h	**9a** (80%)
(7)	**9**	Na_2Se/THF, Rt / 48 h	**9a** (51%)
(8)	**9**	Li_2Se/THF, Rt / 20 h	**9a** (65%)
(9)	**9**	Li_2Te/THF/MeCN[b], Rt / 16 h	**9a** (99%)
(10)	**9**	Na_2Te/MeCN, Rt / 24 h	**9a** (44%)
(11)	 **10** (83%)	Li_2Te / THF, Rt / 48 h	 **10a** (90%)
(12)	 **11** (*ca.* 29%)	Li_2Te / THF, Rt / 24 h	 **9a** (60%)
(13)	 **12** (81%)	Li_2Te/THF, Rt / 14 h	 **12a**[c] (83%)
(14)	**12**	Na_2Te/THF, Rt / 24 h	**12a** (42%)

	Dimesylate (Yield from diol)		Olefin
(15)	 **13** (81%)	Li_2Te/THF, Rt / 96 h	 **13a** (14%)[d]
(16)	 **14** (78%)	Li_2Te/THF, Rt / 20 h	 **14a** (78%)
(17)	 **15** (87%)[e,f]	Li_2Te/THF, Rt / 16 h	 **15a**[e,f,g] (*ca.* 89%)
(18)	 **16** (59%)[f,h]	2.5 equiv Li_2Te, THF / 40°C / 24 h	 **16a** (*ca.* 93%)[f,i]
(19)	 **17** (78%)	Li_2Te/THF, Rt / 12 h[j]	 **17a** (67%)[k]
(20)	 **18** (88%)	Li_2Te/THF, Rt / 17 h	 **18a** (75%)[k]
(21)	 **19** (-%)	Li_2Te/THF, Rt / 12 h	Complex mixture
(22)	 **20** (-%)	Li_2Te/THF, Rt / 12 h	Complex mixture
(23)	 **21** (72%)	Li_2Te/THF, Rt / 12 h	No reaction
(24)	 **22** (92% from diol)	Li_2Te/THF, Rt	No reaction. Starting material recovered in 70% yield

[a] All lithium salts were generated using Et_3BHLi, and sodium salts were prepared from Na and Te (or Se) in liquid NH_3, followed by evaporation of the NH_3. [b] MeCN was added after formation of Li_2Te. [c] Hydrogenation gave the saturated compound (61%). [d] Possibly, the poor yield is due, in part, to reaction of the excess of Et_3BHLi with the acetate group. [e] X = N=CH(NMe_2). [f] DMT = dimethoxytrityl. [g] Hydrogenation and removal of the N-protecting group gave the saturated product in 43% overall yield. [h] Yield not optimized; recycling as previously described for analogous compounds (Kawana, M.; Kuzuhara, H. *J. Chem. Soc., Perkin Trans. 1* **1992**, 469) was not done. [i] Trace impurities are present (^{1}H NMR). [j] Reaction is fast; no starting material remains after 1 h. [k] Yield not optimized.

taminated with polytellurides, as suggested by the generation of an intense dark red or purple color.[26] *Dilithium ditelluride*[25] itself does not lead to olefinic material, at least as judged by attempted reaction with dimesylate **9**. Sodium hydrogen telluride[27] is likewise unsuccessful (with the same compound).

We also tried several electrochemical methods[29] for generating the telluride dianion, but yields of didehydrodideoxynucleosides were very poor. Only with the

(29) Gautheron, B.; Tainturier, G.; Degrand, C. *J. Am. Chem. Soc.* **1985**, *107*, 5579. *Cf.* Degrand, C.; Prest, R. *J. Electroanal. Chem.* **1990**, *282*, 281.

Table 2

entry	reaction mixture	substrate	remarks
1	Te/sodium naphthalenide[28a]	**9**	none of desired olefin
2	Te/Rongalite/aq NaOH[28c,d]	**9**	none of desired olefin
3	Te/Rongalite/DMF/$NaHCO_3$	**9**	none of desired olefin
4	Te/hydrazine/NaOH[28e]	**9**	none of desired olefin
5	Te/hydrazine/LiOH/DMF or THF	none	no reduction of Te
6	Te/$NaBH_4$/THF or DMF[28f−h]	**9**	none of desired olefin
7	Te/Bu_4NBH_4[28d]	**9**	none of desired olefin
8	Te/$LiBH_4$/DMF	none	no reduction of Te
9	Te/Red-Al/THF	**9**	desired olefin (6%)
10	Te/$LiAlH_4$/THF	**9**	no reduction of Te
11	Te/Et_3BHLi; addition of acetone	**9**	desired olefin (30%)
12	Te/Et_3BHLi; addition of EtOH	**9**	desired olefin (38%)
13	Te/DIBAL-H/THF	none	no reduction of Te
14	Te/NaH/DMF or dioxane[28i−k]	**9**	none of desired olefin
15	Te/LiH/THF	**9**	no reduction of Te
16	Te/LiH/Et_3B/THF	**9**	no reduction of Te
17	Se/LiH/THF	**9**	no reduction of Se
18	Te/*s*-Bu_3BHLi	**9**	desired olefin (62%)

simple dimesylate **6** could the desired olefin be isolated (43% yield).

In our standard deoxygenation with Te^{2-}, the Te precipitates at the end of the experiment. In one small-scale test (0.128 mmol of dimesylate **15**), we recovered 53% of the original amount of Te by filtering the crude reaction mixture through a bed of β-cyclodextrin and then dissolving the cyclodextrin in boiling water. Filtration of the hot mixture afforded the Te as a fine powder. In this experiment the initial olefin was processed further: hydrogenation of the double bond and removal of the *N*-protecting group gave 5′-*O*-[bis(4-methoxyphenyl)phenylmethyl]-2′,3′-dideoxyadenosine in 43% yield (over three steps).

Use of Selenide or Sulfide Dianion. Treatment of dimesylate **9** (Table 1, entries 7 and 8) with selenide dianion (from Se and Na/liquid NH_3[30] or Se and Et_3BHLi[31]) does lead to the expected olefin, but the reaction is slower than in the case of Te. An attempt (with **9**) to use sulfide dianion (from S and Et_3BHLi[32]), in the hope of forming an episulfide, gave a complex mixture.

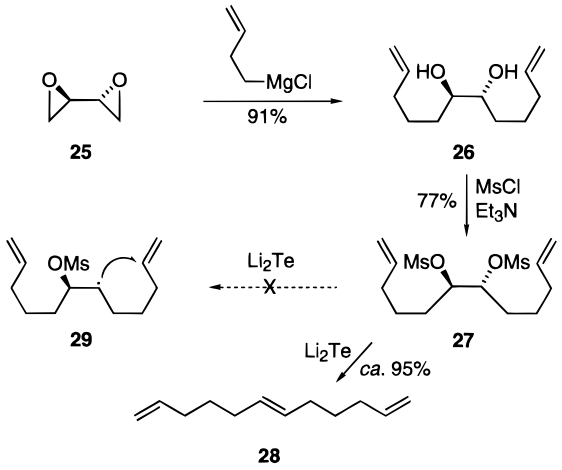
Effect of Solvent and Temperature. We generally used THF, as this solvent is inert to Et_3BHLi. However, when preformed Na_2Te (from Na, Te, and liquid NH_3) is used, either THF or MeCN is suitable. We did not make a careful comparison of yields in the two solvents; we simply established (Table 1, entries 9 and 10) that the desired olefin is obtained in acetonitrile.

We generally ran our experiments at room temperature, and although the reaction is slow, yields are often high (see Table 1).

Nature of the Dimesylate. As shown in Table 1, both terminal and internal acyclic dimesylates undergo the present reaction. In the case of dimesylates derived from cyclic diols, those in the nucleoside series work well—fortunately—but the sugar-derived substrate **22** is not suitable, and it is clear that the hydroxyl groups have to be *syn* coplanar (or close to that). This preferred arrangement is, of course, readily accessible to the acyclic compounds.

The reaction is sensitive to steric factors, and the dimesylate derived from the [2.2.1] bicyclic substrate **21** (Table 1, entry 23) is not converted into olefin—the material is simply recovered. The cyclooctane substrates[23a,33] (Table 1, entries 21 and 22) gave complex mixtures.

Scheme 2



Of the protecting groups used for the 5′-oxygen, only acetyl appears to be unsuitable (Table 1, entry 15).

Mechanistic Considerations. The stereochemical result with the open chain dimesylates **7** and **18**, i.e., the formation of *Z* and *E* olefins, respectively (Table 1, entries 2 and 20), is consistent with a simple nucleophilic displacement mechanism (eq 1), as is the sensitivity of the reaction to steric factors (Table 1, entries 21−23). However, our observations do not exclude a single electron transfer pathway. In an attempt to intercept possible carbon radical intermediates, arising from a SET mechanism, we prepared the dimesylate **27**, as shown in Scheme 2. Under our standard conditions, we were unable to detect any cyclized product and obtained only the olefin **28** (*ca.* 95% yield), whose stereochemistry was established[34] by NMR techniques. Our working hypothesis is, therefore, the simple double nucleophilic pathway.

(30) *Cf.* Rossi, R. A.; Peñéñory, A. B. *J. Org. Chem.* **1981**, *46*, 4580.
(31) Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204.
(32) Gladysz, J. A.; Wong, V. K.; Jick, B. S. *Tetrahedron* **1979**, *35*, 2329.
(33) Durst, T.; Tin, K.-C. *Can. J. Chem.* **1970**, *48*, 845.
(34) The *E*-stereochemistry of the C(6)−C(7) double bond was determined from the value (16 Hz) of the coupling constant of the hydrogens on the double bond. A value of *ca.* 8−10 Hz would be observed if the stereochemistry were *Z*. The measurement was made by first decoupling the hydrogens on the C(5) and C(8) methylene groups to simplify the spectrum. The coupling constant was then measured from the proton satellites corresponding to $R^{13}CH{=}^{12}CHR$. In this situation (i.e., one carbon is ^{13}C and the other is ^{12}C) the molecule is unsymmetrical and the coupling can be measured.

Conclusion

Conversion of vicinal diols into the corresponding dimesylates, followed by treatment with Na_2Te (from Na and Te in liquid NH_3) or Li_2Te (from Te and Et_3BHLi), results in smooth deoxygenation to the olefin in the case of acyclic compounds or nucleosides. With nucleosides, the 5′-protecting group can be removed,[9b,35,36] and hydrogenation[37] of the double bond gives the corresponding dideoxy compounds. Amino groups in the nucleoside base components do not necessarily have to be protected, and in general, the deoxygenation described here is well-suited to the preparation of deoxynucleosides.

Experimental Section

General Procedures. Unless stated to the contrary, the following conditions apply: Reactions were carried out under a slight static pressure of Ar that had been purified by passage through a column (3.5 × 42 cm) of R-311 catalyst[38] and then through a similar column of Drierite. Glassware was dried in an oven for at least 3 h before use (120 °C) and either cooled in a desiccator over Drierite or assembled quickly, sealed with rubber septa, and allowed to cool under a slight static pressure of Ar. Reaction mixtures were stirred by Teflon-coated magnetic stirring bars.

Hexane used for chromatography was distilled before use.

Products were isolated from solution by evaporation under water-aspirator vacuum at, or below, room temperature, using a rotary evaporator.

Cannula transfers were done under slight pressure (Ar), not by suction.

Commercial thin layer chromatography (TLC) plates (silica gel, Merck 60F−254) were used. Spots were detected by spraying the plate with a solution of phosphomolybdic acid[39] or *p*-anisaldehyde,[40] followed by charring with a heat gun or by examination under UV light. Silica gel for flash chromatography was Merck type 60 (230−400 mesh).

Dry solvents were prepared under an inert atmosphere and transferred by syringe or cannula. Dry THF and Et_2O were distilled from sodium and benzophenone ketyl. MeCN and pyridine were distilled from CaH_2.

FTIR measurements were made as casts from the specified solvent using potassium bromide plates.

The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate zero, one, two, or three attached hydrogens, respectively.

Preparation of Sodium Telluride (Na_2Te).[41] A 500-mL three-neck round-bottomed flask was charged with Te powder (200 mesh, 2.205 g, 17.28 mmol) and a stirring bar. Na (794 mg, 34.5 mmol) was placed in a sidearm addition tube, and the central neck of the flask was fitted with a condenser charged with dry ice/acetone and closed by a septum carrying both an entry needle for Ar and an exit needle leading to an oil bubbler. The third neck of the flask was temporarily closed by a septum, and the flask was flushed with Ar. The septum in the third neck was removed and immediately replaced by an adaptor (fitted with a tap) connected to a tank of liquid NH_3. The flask was then cooled with dry ice/MeCN, and NH_3 was led in until *ca.* 200 mL had collected. The ammonia inlet was closed, and a slow stream of Ar was maintained. The stirrer was started, and the Na was added portionwise by tapping the sidearm addition tube. The mixture changed from red to bluish-green to white, by which stage formation of Na_2Te was complete. The cooling bath was removed, and stirring was continued overnight, during which time the coolant in the condenser attained room temperature and the NH_3 evaporated. The resulting beige Na_2Te (*ca.* 100% yield) was transferred in an Ar-filled glovebag to a storage flask.

The experiment was also done on a larger scale (Te, 6.096 g) with the same result.

Preparation of Sodium Selenide (Na_2Se).[30] A 500-mL three-neck round-bottomed flask was charged with Se powder (325 mesh, 2.847 g, 36.06 mmol) and a stirring bar. Na (1.741 g, 75.73 mmol) was placed in a sidearm addition tube, and the central neck of the flask was fitted with a condenser charged with dry ice/acetone and closed by a septum carrying both an entry needle for Ar and an exit needle leading to an oil bubbler. The third neck of the flask was temporarily closed by a septum, and the flask was flushed with Ar. The septum in the third neck was removed and immediately replaced by an adaptor (fitted with a tap) connected to a flask containing a small amount (*ca.* 1 g) of Na. This latter flask was, in turn, connected to a tank of liquid NH_3 and was then cooled with dry ice/MeCN. NH_3 was led in until *ca.* 200 mL had collected. The cooling bath was removed, and the NH_3 was distilled into the reaction vessel, which was cooled with dry ice/MeCN. The ammonia inlet was removed, and a slow stream of Ar was maintained. The stirrer was started, and the Na was added portionwise by tapping the sidearm addition tube. The mixture changed color and eventually became white, by which stage formation of Na_2Se was complete. The cooling bath was removed, and stirring was continued overnight, during which time the coolant in the condenser attained room temperature and the NH_3 evaporated. The resulting slightly orange Na_2Se (*ca.* 100% yield) was transferred in an Ar-filled glovebag to a storage flask.

4-(1-Naphthyl)butane-1,2-diol. OsO_4 (1.7 mL, 2.5% w/w solution of OsO_4 in *t*-BuOH) was added to a stirred solution of 1-(3-butenyl)naphthalene[42] (**6a**) (1.121 g, 6.153 mmol) and 4-methylmorpholine *N*-oxide (1.033 g, 7.652 mmol) in acetone (30 mL) and water (15 mL). Stirring at room temperature was continued for 43 h. EtOAc (100 mL) was then added, and the organic layer was washed with water (1 × 100 mL) and aqueous Na_2SO_3 (10% w/v, 2 × 50 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (5 × 20 cm), using 7:3 EtOAc−hexane, gave 4-(1-naphthyl)-butane-1,2-diol (1.200 g, 90%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3360 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.70−2.05 (m, 4 H), 3.05−3.45 (m, 2 H), 3.50 (dd, J = 11.0, 7.0 Hz, 1 H), 3.71 (dd, J = 11.0, 3.0 Hz, 1 H), 3.75−3.95 (m, 1 H), 7.30−7.60 (m, 4 H), 7.60−7.80 (m, 1 H), 7.80−7.95 (m, 1 H), 7.95−8.20 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.93, 34.02, 66.86, 71.89, 123.74, 125.55, 125.58, 125.92, 126.07, 126.82, 128.85, 131.81, 133.97, 137.89; exact mass m/z calcd for $C_{14}H_{16}O_2$ 216.1151, found 216.1151.

4-(1-Naphthyl)butane-1,2-diol Bis(methanesulfonate) (6). $MeSO_2Cl$ (1.6 mL, 20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred and cooled (0 °C) solution of 4-(1-naphthyl)butane-1,2-diol (1.123 g, 5.192 mmol) and pyridine (3.4 mL, 41 mmol) in CH_2Cl_2 (10 mL). The ice bath was removed, and stirring was continued for 16 h. The mixture was poured onto ice (*ca.* 50 g) and extracted with EtOAc (1 × 100 mL). The organic extract was washed with aqueous $CuSO_4$ (10% w/v, 2 × 50 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 30 cm), using 1:1 EtOAc−hexane, gave **6** (1.849 g, 96%) as a colorless oil: FTIR (CH_2Cl_2 cast) 1356, 1173 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.05−2.40 (m, 2 H), 3.0−3.10 (s, 3 H), 3.10−3.15 (s, 3 H), 3.15−3.45 (m, 2 H), 4.30 (dd, J = 11.0, 6.0 Hz, 1 H), 4.44 (dd, J = 11.0, 3.0 Hz, 1 H), 4.95−5.10 (m, 1 H),

(35) (a) Cosford, N. D. P.; Schinazi, R. F. *J. Org. Chem.* **1991**, *56*, 2161. (b) Cosford, N. D. P.; Schinazi, F. *Nucleosides Nucleotides* **1993**, *12*, 149.

(36) E.g. (a) Kaskar, B.; Markovac, A. *J. Heterocycl. Chem.* **1989**, *26*, 1531. Removal of 5′-*O*-trityl and acyl groups from 3′-deoxythymidine: (b) Sekine, M.; Nakanishi, T. *J. Org. Chem.* **1990**, *55*, 924.

(37) Manchand, P. S.; Belica, P. S.; Holman, M. J.; Huang, T.-N.; Maehr, H.; Tam, S. Y.-K.; Yang, R. T. *J. Org. Chem.* **1992**, *57*, 3473.

(38) Supplied by Chemical Dynamics Corp., South Plainfield, NJ.

(39) Phosphomolybdic acid (15 g) and $(NH_4)_2Ce(NO_3)_6$ (2.5 g) dissolved in a mixture of water (485 mL) and concentrated H_2SO_4 (15 mL).

(40) *p*-Anisaldehyde (15 drops) was added to concentrated H_2SO_4 (6 mL) and EtOH (94 mL).

(41) *Cf.* Brauer, G., Ed. *Handbuch der Präparativen Anorganischen Chemie*; Ferdinand Enke: Stuttgart, 1975; Vol. I, p 431.

(42) Lambert, J. B.; Fabricius, D. M.; Hoard, J. A. *J. Org. Chem.* **1979**, *44*, 1480. In preparing the butenylnaphthalene, we used allyllithium, generated (Seyferth, D.; Weiner, M. A.; *J. Org. Chem.* **1961**, *26*, 4797) from triphenyl(2-propenyl)stannane.

7.30−7.65 (m, 4 H), 7.70−7.80 (m, 1 H), 7.80−7.93 (m, 1 H), 7.93−8.05 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.25, 32.08, 37.74, 38.90, 69.46, 78.66, 123.26, 125.63, 125.76, 126.30 (two overlapping signals), 127.40, 129.01, 131.49, 134.00, 135.99; exact mass *m*/*z* calcd for $C_{16}H_{20}O_6S_2$ 372.0702, found 372.0694.

General Procedure for Deoxygenation: 1-(3-Butenyl)-naphthalene (6a) from Dimesylate 6. Te powder (200 mesh, 167 mg, 1.31 mmol) and a small stirring bar were placed in a dry round-bottomed flask fused onto a reflux condenser. The flask was closed with a septum and flushed with Ar. A solution of Et_3BHLi (1 M in THF, 3.4 mL, 3.4 mmol) was injected, and the mixture was stirred until a milky white suspension had formed (*ca.* 5 h). 4-(1-Naphthyl)butane-1,2-diol bis(methanesulfonate) (**6**) (488 mg, 1.31 mmol) in THF (5 mL) was then injected dropwise, and the mixture was stirred for 20 h. The mixture was washed out of the flask with acetone and evaporated at room temperature. Flash chromatography of the residue over silica gel (2 × 30 cm), using hexane, gave **6a** (210 mg, 88%), spectroscopically identical to an authentic sample.

Benzyl (9*RS*,10*SR*)-9,10-Dihydroxyoctadecanoate. (a) Oleic Acid Benzyl Ester (7a). The following procedure is different from that given in the literature.[43]

BnOH (2.59 g, 24.0 mmol) was added to a stirred solution of oleic acid (5.70 g, 20.2 mmol) and TsOH. H_2O (200 mg, 0.6 mmol) in PhH (20 mL). The mixture was refluxed for 22 h using a Dean−Stark apparatus. Evaporation of the solvent and flash chromatography of the residue over silica gel (6 × 40 cm), using first hexane and then 1:9 EtOAc−hexane, gave **7a** (7.55 g, 100%) as a colorless oil: FTIR (CH_2Cl_2, cast) 2925, 2853, 1739 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80−0.98 (m, 3 H), 1.08−1.45 (m, 20 H), 1.52−1.75 (m, 2 H), 1.90−2.01 (m, 4 H), 2.30−2.42 (apparent t, J = 8.0 Hz, 2 H), 5.12 (apparent s, 2 H), 5.30−5.40 (m, 2 H), 7.30−7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.13, 22.71, 24.98, 27.26, 29.02, 29.13, 29.17, 29.28, 29.36, 29.49, 29.56, 29.62, 29.80, 31.94, 34.36, 66.07, 128.17 (two overlapping signals), 128.55, 129.77, 130.02, 136.21, 173.64; mass (CI) *m*/*z* calcd for $C_{25}H_{40}O_2$ 372, found 372.

(b) Benzyl (9*RS*,10*SR*)-9,10-Dihydroxyoctadecanoate. OsO_4 (3.95 mL, 2.5% w/w solution of OsO_4 in *t*-BuOH) was added to a solution of oleic acid benzyl ester (5.658 g, 15.18 mmol) and 4-methylmorpholine *N*-oxide (3.749 g, 27.77 mmol) in acetone (500 mL) and water (38 mL). The mixture was stirred at room temperature for 24 h and then evaporated at room temperature to *ca.* 100 mL. EtOAc (200 mL) was added, and the organic layer was washed with water (1 × 200 mL) and aqueous Na_2SO_3 (10% w/v, 3 × 200 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (10 × 50 cm), using 3.2:96.8 MeOH−$CHCl_3$, gave benzyl (9*RS*,10*SR*)-9,10-dihydroxyoctadecanoate (4.432 g, 72%) as a colorless oil: FTIR ($CHCl_3$, cast) 3280, 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.80−1.00 (m, 3 H), 1.20−1.58 (m, 24 H), 1.58−1.75 (m, 2 H), 1.95 (br s, 2 H), 2.35 (t, J = 7.2, 2 H), 3.50−3.70 (m, 2 H), 5.11 (s, 2 H), 7.28−7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.13, 22.70, 24.93, 25.95, 26.06, 29.06, 29.18, 29.31, 29.46, 29.59, 29.73, 31.21, 31.30, 31.91, 34.34, 66.12, 74.69, 74.76, 128.20 (two overlapping signals), 128.58, 136.70, 173.70; exact mass *m*/*z* calcd for $C_{25}H_{38}O_2$ (M − $2H_2O$) 370.2873, found 370.2869; mass (CI) *m*/*z* calcd for $C_{25}H_{42}O_4$ 406, found 424 (M + 18).

Benzyl (9*RS*,10*SR*)-9,10-Dihydroxyoctadecanoate Bis(methanesulfonate) (7). $MeSO_2Cl$ (1.8 mL, 23 mmol) in $CHCl_3$ (4 mL) was added dropwise to a stirred and cooled (0 °C) solution of benzyl (9*RS*,10*SR*)-9,10-dihydroxyoctadecanoate (1.170 g, 2.878 mmol) and pyridine (3.80 mL, 46.0 mmol) in $CHCl_3$ (11 mL). The ice bath was removed, and stirring was continued for 40 h. The mixture was poured onto ice (*ca.* 50 g) and extracted with $CHCl_3$ (200 mL). The organic extract was washed with aqueous $CuSO_4$ (10% w/v, 2 × 100 mL) and aqueous NaOH (0.5 M, 1 × 50 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 30 cm), using 1:19 MeOH−$CHCl_3$, gave **7** (1.532 g, 95%), which contained a trace impurity (^{1}H NMR, 200 MHz, small signals at δ 3.0 and 3.1) but was suitable for the next stage: FTIR ($CHCl_3$, cast) 1735, 1357, 1175 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.78−0.98 (m, 3 H), 1.18−1.88 (m, 26 H), 2.35 (t, J = 7.0 Hz, 2 H), 3.09 (s, 6 H), 4.68−4.88 (m, 2 H), 5.10 (s, 2 H), 7.25−7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.07, 22.50, 22.61, 24.81, 25.36, 25.45, 28.91 (three overlapping signals), 29.14, 29.27, 29.58, 29.65, 31.77, 34.22, 38.82 (two overlapping signals), 66.06, 82.81, 82.91, 128.15 (two overlapping signals), 128.54, 136.14, 173.52; exact mass *m*/*z* calcd for $C_{27}H_{47}O_8S_2$ (M + H) 563.2714, found 563.2732.

Oleic Acid Benzyl Ester (7a) from Dimesylate 7. (a) Use of Li_2Te. Apart from a change in solvent, the general procedure was followed, using Te powder (200 mesh, 53 mg, 0.412 mmol), Et_3BHLi (1 M in THF, 0.78 mL, 0.78 mmol), dimesylate **7** (108 mg, 0.192 mmol) in dioxane (5 mL), and a reaction time of 14 h. Starting material was still present (TLC, silica, 40:60 CH_2Cl_2−hexane), and so the mixture was heated at 100 °C for 2 h (TLC control). The mixture was cooled, washed out of the flask with hexane, and evaporated at room temperature. Flash chromatography of the residue over silica gel (1.5 × 20 cm), using 2:3 CH_2Cl_2−hexane, gave **7a** (59 mg, 83%) as a colorless oil, spectroscopically identical to an authentic sample.

(b) Use of Li_2Se. Se powder (325 mesh, 29 mg, 0.360 mmol) and a small stirring bar were placed in a dry round-bottomed flask fused onto a reflux condenser. The flask was closed with a septum and flushed with Ar. A solution of Et_3BHLi (1 M in THF, 0.68 mL, 0.68 mmol) was injected, and the mixture was stirred until a milky white suspension had formed (*ca.* 20 min). Dimesylate **7** (101 mg, 0.179 mmol) in dioxane (5 mL) was then injected dropwise, and the mixture was stirred for 24 h. Starting material was still present (TLC, silica, 40:60 CH_2Cl_2−hexane), and so the mixture was heated at 100 °C for 4 h. The mixture was cooled, washed out of the flask with hexane, and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 30 cm), using 7:13 CH_2Cl_2−hexane, gave **7a** (50.8 mg, 76%) as a colorless oil, spectroscopically identical to an authentic sample.

Methyl 5-*O*-Benzyl-2,3-di-*O*-mesyl-*β*-D-ribofuranoside (8). $MeSO_2Cl$ (1.6 mL, 20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred and cooled (0 °C) solution of methyl 5-*O*-benzyl-*β*-D-ribofuranoside[44] (1.302 g, 5.122 mmol) and pyridine (3.3 mL, 41 mmol) in CH_2Cl_2 (10 mL). The ice bath was removed, and stirring was continued for 24 h. The mixture was poured onto ice (*ca.* 50 g) and extracted with EtOAc (100 mL). The organic extract was washed with aqueous $CuSO_4$ (10% w/v, 2 × 50 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 30 cm), using 3:7 EtOAc−hexane, gave **8** (1.963 g, 93%) as a colorless oil: FTIR (CH_2Cl_2, cast) 1384, 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.97 (s, 3 H), 3.15 (s, 3 H), 3.41 (s, 3 H), 3.62 (dd, J = 10.5, 5.0 Hz, 1 H), 3.70 (dd, J = 10.5, 4.4 Hz, 1 H), 4.40 (ddd, J = 6.5, 5.0, 4.5 Hz, 1 H), 4.58 (q, J = 17.0, 12.0 Hz, 2 H), 4.98 (dd, J = 5.0, 1.5 Hz, 1 H), 5.08 (d, J = 1.5 Hz, 1 H), 5.20 (dd, J = 6.5, 5.0 Hz, 1 H), 7.28−7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 38.12, 38.50, 55.65, 69.79, 73.74, 77.26, 79.15, 79.79, 105.68, 127.91, 128.02, 128.54, 137.49; exact mass *m*/*z* calcd for $C_{15}H_{22}O_9S_2$ 410.0706, found 410.0734.

Methyl 5-*O*-Benzyl-2,3-dideoxy-*β*-D-pent-2-enofuranoside (8a) from Dimesylate 8. The general procedure was followed, but at a different temperature for the second stage, using Te powder (200 mesh, 72 mg, 0.565 mmol), Et_3BHLi (1 M in THF, 1.27 mL, 1.27 mmol), and methyl 5-*O*-benzyl-2,3-di-*O*-mesyl-*β*-D-ribofuranoside (**8**) (100 mg, 0.244 mmol) in dioxane (5 mL). The mixture was refluxed for 20 h. At this stage all of the dimesylate had reacted (TLC, silica, 30:70 EtOAc−hexane). The mixture was cooled, washed out of the

(43) Shonle, H. A.; Row, P. Q. *J. Am. Chem. Soc.* **1921**, *43*, 361.

(44) Using literature procedures, methyl 2,3-*O*-isopropylidene-*β*-D-ribofuranoside (Levene, P. A.; Stiller, E. T. *J. Biol. Chem.* **1934**, *104*, 299. Barrett, A. G. M.; Lebold, S. A. *J. Org. Chem.* **1990**, *55*, 3853) was converted into its 5-*O*-benzyl derivative (Tener, G. M.; Khorana, H. G. *J. Am. Chem. Soc.* **1957**, *79*, 437) and then into methyl 5-*O*-benzyl-*β*-D-ribofuranoside (Kawana, M.; Kuzuhara, H.; Emoto, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1492).

flask with acetone, and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 20 cm), using 1:9 EtOAc−hexane, gave **8a** (37 mg, 69%) as a colorless oil: FTIR (neat film) unexceptional; ^{1}H NMR identical to that reported;[45] ^{13}C NMR (acetone-d_6, 75.5 MHz) δ 54.25, 73.54, 74.38, 85.31, 110.06, 128.11, 128.24, 128.33, 128.97, 133.74, 139.66; mass (CI) m/z calcd for $C_{13}H_{16}O_3$ 220, found 220.

5′-*O*-(Triphenylmethyl)uridine 2′,3′-Bis(methanesulfonate) (9). (a) 5′-*O*-(Triphenylmethyl)uridine. The literature procedure[46] was followed, but using a different workup.

Uridine (155 mg, 0.634 mmol), trityl chloride (199 mg, 0.715 mmol), and a small stirring bar were placed in a dry round-bottomed flask fused onto a reflux condenser. The flask was closed with a septum and flushed with Ar. Pyridine (1.90 mL) was injected, and the mixture was stirred at room temperature for 48 h. The mixture was then heated for 30 min (oil bath at 100 °C), cooled, and poured onto ice (*ca.* 25 g). The gummy product was filtered off, washed with water, and dissolved in acetone. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 30 cm), using 1:19 MeOH−CH_2Cl_2, gave 5′-*O*-(triphenylmethyl)uridine (250 mg, 81%): mp 199−200 °C (lit.[46] mp 198−201 °C); FTIR (CH_2Cl_2, cast) 3600−3200, 1691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.35−3.62 (m, 3 H), 4.10−4.25 (m, 1 H), 4.30−4.52 (m, 2 H), 5.25−5.38 (m, 1 H), 5.48−5.65 (br s, 1 H), 5.85−5.93 (m, 1 H), 7.18−7.50 (m, 15 H), 7.95−8.06 (apparent d, J = 8.0 Hz, 1 H), 10.35−10.45 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 62.01, 69.71, 75.59, 83.80, 87.67, 90.88, 102.24, 127.48, 127.77, 128.09, 140.38, 143.24, 151.09, 163.77 (several signals of the trityl group overlap); exact mass m/z calcd for $C_{19}H_{15}$ (M − $C_9H_{11}N_2O_6$) 243.1174, found 243.1171; exact mass m/z calcd for $C_9H_{11}N_2O_6$ (M − $C_{19}H_{15}$) 243.0617, found 243.0620; mass (FAB) m/z calcd for $C_{28}H_{27}N_2O_6$ (M + H) 487, found 487.

(b) 5′-*O*-(Triphenylmethyl)uridine 2′,3′-Bis(methanesulfonate) (9). $MeSO_2Cl$ (3.78 mL, 48.9 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise to a stirred and cooled (0 °C) solution of 5′-*O*-(triphenylmethyl)uridine (5.944 g, 12.22 mmol) and dry pyridine (7.9 mL, 98 mmol) in dry CH_2Cl_2 (25 mL). The ice bath was removed, and stirring was continued for 15 h. The mixture was poured onto ice (*ca.* 200 g) and extracted with EtOAc (2 × 200 mL). The organic extract was washed with water (2 × 100 mL), aqueous NaOH (0.5 M, 2 × 100 mL), and aqueous $CuSO_4$ (10% w/v, 1 × 200 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue twice over silica gel (5 × 35 cm), using 1:49 MeOH−CH_2Cl_2 for the first chromatography and 1:99 MeOH−CH_2Cl_2 for the second, gave **9**[47] (5.837 g, 74%) as a colorless oil.

Another experiment, run on a smaller scale [5′-*O*-(triphenylmethyl)uridine, 2.282 g] gave the product in 86% yield: FTIR (CH_2Cl_2, cast) 1694, 1364, 1179 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.10 (s, 3 H), 3.21 (s, 3 H), 3.50−3.75 (m, 2 H), 4.25−4.50 (m, 1 H), 5.25−5.65 (m, 3 H), 6.02 (d, J = 3.0 Hz, 1 H), 7.10−7.60 (m, 15 H), 7.72 (d, J = 8.0 Hz, 1 H), 9.32 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 38.62, 38.86, 60.87, 73.58, 78.24, 80.93, 88.18, 88.43, 103.20, 127.69, 128.24, 128.73, 139.95, 142.68, 150.49, 163.02 (several signals of the trityl group overlap); mass (HRFAB) m/z calcd for $C_{30}H_{31}N_2O_{10}S_2$ (M + H) 643.1412, found 643.1401.

2′,3′-Didehydro-2′,3′-dideoxy-5′-*O*-(triphenylmethyl)uridine (9a) from Dimesylate 9. (a) Use of Na_2Te. Na_2Te (1.796 g, 10.35 mmol) (prepared from the elements, as described above) and a small stirring bar were placed in a dry 100-mL round-bottomed flask closed with a septum. The flask was flushed with Ar. Dimesylate **9** (2.660 g, 4.139 mmol) in dry THF (40 mL) was then injected, and the mixture was stirred for 20 h at room temperature. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (4 × 30 cm), using 11:5:4 CH_2Cl_2−PhMe−MeCN, gave **9a** (1.402 g, 75%) as a colorless oil, spectroscopically identical to an authentic[9b] sample.

Another experiment, run on a smaller scale (dimesylate, 139 mg), gave the product in 93% yield.

(b) Use of Li_2Te in Dioxane−THF. Apart from a change in solvent, the general procedure was followed, using Te powder (200 mesh, 40 mg, 0.313 mmol), Et_3BHLi (1 M in THF, 0.66 mL, 0.66 mmol), dimesylate **9** (100 mg, 0.155 mmol) in dioxane (5 mL), and a reaction time of 48 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (2 × 25 cm), using 10:7:3 CH_2Cl_2−PhMe−MeCN, gave **9a** (56 mg, 80%) as a colorless oil, spectroscopically identical to an authentic sample.

(c) Use of Na_2Se. Na_2Se (30 mg, 0.241 mmol) (prepared from the elements, as described above) and a small stirring bar were placed in a dry round-bottomed flask fused onto a reflux condenser. The flask was closed with a septum and flushed with Ar. Dimesylate **9** (59 mg, 0.092 mmol) in THF (2 mL) was then injected, and the mixture was stirred for 48 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue twice over silica gel (1 × 25 cm), using 11:5:4 CH_2Cl_2−PhMe−MeCN, gave **9a** (21.3 mg, 51%) as a colorless oil, spectroscopically identical to an authentic sample.

(d) Use of Li_2Se. Se powder (325 mesh, 15 mg, 0.187 mmol) and a small stirring bar were placed in a dry round-bottomed flask fused onto a reflux condenser. The flask was closed with a septum and flushed with Ar. A solution of Et_3BHLi (1 M in THF, 0.37 mL, 0.37 mmol) was injected, and the mixture was stirred for *ca.* 4 h. A milky white suspension was formed after 10 min. Dimesylate **9a** (59 mg, 0.093 mmol) in THF (3 mL) was then injected dropwise, and the mixture was stirred for 20 h. The mixture turned brown on initial addition of the dimesylate solution. The mixture was washed out of the flask with CH_2Cl_2, K_2CO_3 (500 mg) was added, and the mixture was then evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 20 cm), using 10:7:3 CH_2Cl_2−PhMe−MeCN, gave **9a** (27 mg, 65%) as a colorless oil, spectroscopically identical to an authentic sample.

(e) Use of Li_2Te in the Presence of Acetonitrile. Apart from a change in solvent, the general procedure was followed, using Te powder (200 mesh, 42 mg, 0.327 mmol), Et_3BHLi (1 M in THF, 0.73 mL, 0.73 mmol), dimesylate **9** (100 mg, 0.155 mmol) in dry MeCN (2 mL), and a reaction time of 16 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 30 cm), using 11:5:4 CH_2Cl_2−PhMe−MeCN, gave **9a** (70 mg, 99%) as a colorless oil, spectroscopically identical to an authentic sample.

(f) Use of Na_2Te in the Presence of MeCN. Dimesylate **9** (1.287 g, 2.003 mmol) in MeCN (40 mL) was added to Na_2Te (869 mg, 5.01 mmol, weighed out in a glove bag), and the mixture was stirred at room temperature for 24 h (Ar atmosphere). Evaporation of the solvent and flash chromatography of the residue over silica gel (4 × 20 cm), using 11:5:4 CH_2Cl_2−PhMe−MeCN, gave **9a** (400 mg, 44%) as a colorless oil, spectroscopically identical to an authentic sample.

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(49) Fox, J. J.; Yung, N.; Bendich, A. *J. Am. Chem. Soc.* **1957**, *79*, 2775. We prepared the compound (59% yield) by the literature procedure but ran the reaction at room temperature (24 h). The compound had: FTIR (CH_2Cl_2, cast) 3600−3200, 1691 cm^{-1}; ^{1}H NMR (acetone-d_6, 200 MHz) δ 1.48 (apparent s, 3 H), 3.35−3.48 (m, 2 H), 4.08−4.18 (m, 1 H), 4.32−4.48 (m, 3 H), 4.68−4.77 (m, 1 H), 5.90−6.02 (d, J = 4.0 Hz, 1 H), 7.22−7.62 (m, 16 H), 10.02 (br s, 1 H); ^{13}C NMR (pyridine-d_5, 100.6 MHz) δ 12.41, 64.55, 71.50, 75.36, 84.10, 87.51, 90.06, 110.72, 127.61*, 128.38*, 129.17*, 136.05, 144.37*, 152.13, 164.83 (the four starred signals represent 18 carbons in trityl group); exact mass m/z calcd for $C_{29}H_{26}N_2O_5$ (M − H_2O) 482.1842, found 482.1843.

5-Methyl-5′-*O*-(triphenylmethyl)uridine 2′,3′-Bis(methanesulfonate) (10). The following procedure differs from the reported one.[48]

$MeSO_2Cl$ (0.11 mL, 1.4 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a stirred and cooled (0 °C) solution of 5-methyl-5′-*O*-(triphenylmethyl)uridine[49] (174 mg, 0.348 mmol) and pyridine (0.46 mL, 5.6 mmol) in CH_2Cl_2 (3 mL). The ice bath was removed, and stirring was continued for 48 h. The mixture was poured onto ice (*ca.* 50 g) and extracted with EtOAc (2 × 50 mL). The organic extract was washed with water (2 × 50 mL), aqueous NaOH (0.1 M, 1 × 50 mL), and aqueous $CuSO_4$ (10% w/v), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 30 cm), using 3:97 MeOH−CH_2Cl_2, gave **10** (190 mg, 83%): mp 108−112 °C (lit.[48] mp 107−110 °C); FTIR (CH_2Cl_2, cast) 1693, 1364, 1180 cm^{-1}; ^1H NMR identical to that reported;[48] ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 11.75, 38.68, 38.84, 61.92, 74.96, 77.24, 81.48, 87.83, 88.23, 112.38, 127.71, 128.22, 128.77, 135.31, 142.92, 150.64, 163.39 (several signals of the trityl group overlap); mass (HRFAB) *m*/*z* calcd for $C_{31}H_{33}N_2O_{10}S_2$ (M + H) 657.1578, found 657.1548.

2′,3′-Didehydro-2′,3′-dideoxy-5-methyl-5′-*O*-(triphenylmethyl)uridine (10a) from Dimesylate 10. The general procedure was followed, using Te powder (200 mesh, 25 mg, 0.195 mmol), Et_3BHLi (1 M in THF, 0.50 mL, 0.50 mmol), dimesylate **10** (60 mg, 0.092 mmol) in THF (3 mL), and a reaction time of 48 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (2 × 30 cm), using 10:7:3 CH_2Cl_2−PhMe−MeCN, gave **10a** (38.6 mg, 90%): FTIR (CH_2Cl_2, cast) 1689 cm^{-1}; ^1H NMR identical to that reported;[35b] ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 11.40, 64.96, 85.72, 87.03, 89.71, 111.28, 126.35, 127.41, 127.97, 128.79, 134.56, 136.03, 143.25, 150.80, 163.82 (several signals of the trityl group overlap); exact mass *m*/*z* calcd for $C_{20}H_{17}O$ (M − $C_9H_9N_2O_3$) 273.1279, found 273.1281; exact mass *m*/*z* calcd for $C_9H_9N_2O_3$ (M − $C_{20}H_{17}O$) 193.0613, found 193.0611.

5′-*O*-(Triphenylmethyl)uridine 2′,3′-Bis(*p*-toluenesulfonate) (11). *p*-TsCl (470 mg, 1.47 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a stirred and cooled (0 °C) solution of 5′-*O*-(triphenylmethyl)uridine[46] (200 mg, 0.411 mmol), pyridine (0.80 mL, 9.9 mmol), and 4-(dimethylamino)pyridine (5 mg) in CH_2Cl_2 (2 mL). The ice bath was removed, stirring was continued for 24 h, and the mixture was then heated at 50 °C for a further 24 h. The mixture was cooled, poured onto ice (*ca.* 25 g), and extracted with CH_2Cl_2 (1 × 100 mL). The organic extract was washed with aqueous $CuSO_4$ (10% w/v, 2 × 50 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 30 cm), using 11:5:4 CH_2Cl_2−PhMe−MeCN, gave **11** (93 mg, 29%) as a colorless oil, which was used in the next step without full characterization: ^1H NMR ($CDCl_3$, 200 MHz) δ 2.40 (s, 3 H), 2.45 (s, 3 H), 3.30−3.50 (m, 2 H), 4.30−4.45 (m, 1 H), 5.00−5.35 (m, 3 H), 6.10 (d, *J* = 6.0 Hz, 1 H), 7.15−7.45 (m, 20 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.96 (br s, 1 H).

2′,3′-Didehydro-2′,3′-dideoxy-5′-*O*-(triphenylmethyl)uridine (9a) from Bis(*p*-toluenesulfonate) 11. The general procedure was followed, using Te powder (200 mesh, 12 mg, 0.092 mmol), Et_3BHLi (1 M in THF, 0.21 mL, 0.21 mmol), ditosylate **11** (34.8 mg, 0.0438 mmol) in THF (1 mL), and a reaction time of 24 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 30 cm), using 10:5:4 CH_2Cl_2−PhMe−MeCN, gave **9a** (11.8 mg, 60%) as a colorless oil, spectroscopically identical to an authentic sample.

***N*-Acetyl-5′-*O*-(triphenylmethyl)cytidine.** A very similar procedure (reaction temperature 110 °C) has been reported,[50] but the yield was only 14%.

Pyridine (10 mL) was injected onto a stirred mixture of *N*-acetylcytidine[51] (1.000 g, 3.506 mmol) and trityl chloride (1.075 g, 3.856 mmol), and stirring was continued for 36 h (Ar atmosphere). The mixture was evaporated, diluted with CH_2Cl_2, and again evaporated. The gummy residue was washed with water, and the residue was dissolved in acetone. The solution was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4.5 × 30 cm), using 7:93 MeOH−CH_2Cl_2, gave *N*-acetyl-5′-*O*-(triphenylmethyl)-cytidine (1.475 g, 80%) as a colorless oil: FTIR (CH_2Cl_2, cast) 3600−3200, 1656 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.25 (s, 3 H), 3.30−3.55 (m, 3 H), 4.30−4.48 (m, 3 H), 5.58 (br s, 1 H), 5.80−5.90 (m, 1 H), 7.20−7.40 (m, 16 H), 8.10−8.20 (d, *J* = 8.0 Hz, 1 H), 8.55−8.77 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 24.81, 62.12, 69.88, 76.02, 84.04, 87.44, 92.24, 96.98, 127.32, 127.98, 128.57, 143.18, 144.73, 156.23, 162.64, 170.74 (several signals of the trityl group overlap); exact mass *m*/*z* calcd for $C_{30}H_{27}N_3O_5$ (M − H_2O) 509.1951, found 509.1943.

***N*-Acetyl-5′-*O*-(triphenylmethyl)cytidine 2′,3′-Bis(methanesulfonate) (12).** $MeSO_2Cl$ (0.061 mL, 0.786 mmol) in CH_2Cl_2 (0.6 mL) was added dropwise to a stirred and cooled (0 °C) solution of *N*-acetyl-5′-*O*-(triphenylmethyl)cytidine (104 mg, 0.196 mmol) and Et_3N (0.060 mL, 0.434 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at 0 °C for 25 min, poured onto ice (*ca.* 100 g), and extracted with CH_2Cl_2 (100 mL). The organic extract was washed with water (1 × 100 mL), saturated aqueous $NaHCO_3$ (1 × 100 mL), and water (1 × 100 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 30 cm), using 3.5:96.5 MeOH−CH_2Cl_2, gave **12** (108 mg, 81%): FTIR (CH_2Cl_2, cast) 1722, 1666, 1490, 1366, 1181 cm^{-1}; ^1H NMR (CD_2Cl_2, 200 MHz) δ 2.18 (s, 3 H), 3.06 (s, 3 H), 3.35 (s, 3 H), 3.56 (dd, *J* = 11.5, 2.2 Hz, 1 H), 3.68 (dd, *J* = 11.5, 2.2 Hz, 1 H), 4.30−4.50 (m, 1 H), 5.37−5.55 (m, 2 H), 5.97 (br s, 1 H), 7.10 (d, *J* = 7.0 Hz, 1 H), 7.20−7.60 (m, 15 H), 8.25 (d, *J* = 7.0 Hz, 1 H), 8.90 (br s, 1 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 25.01, 38.90, 39.24, 60.49, 72.58, 79.89, 80.58, 88.22, 90.44, 97.46, 127.87, 128.47, 129.02, 143.30, 144.85, 155.29, 163.71, 171.23 (several signals of the trityl group overlap); mass (HRFAB) *m*/*z* calcd for $C_{32}H_{34}N_3O_{10}S_2$ (M + H) 684.1687, found 684.1651.

***N*-Acetyl-2′,3′-didehydro-2′,3′-dideoxy-5′-*O*-(triphenylmethyl)cytidine (12a) from Dimesylate 12. (a) Use of Li_2Te.** The general procedure was followed, using Te powder (200 mesh, 39 mg, 0.307 mmol), Et_3BHLi (1 M in THF, 0.66 mL, 0.66 mmol), *N*-acetyl-5′-*O*-(triphenylmethyl)cytidine 2′,3′-dimethanesulfonate (100 mg, 0.146 mmol) in THF (2 mL), and a reaction time of 14 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 15 cm), using 5:3:2 MeCN−CH_2Cl_2−PhMe, gave **12a** (60 mg, 83%) as a colorless oil containing trace impurities (^1H NMR, 200 MHz): FTIR (CH_2Cl_2, cast) 1722, 1672 cm^{-1}; ^1H NMR (CD_2Cl_2, 200 MHz) δ 2.18 (s, 3 H), 3.30−3.50 (m, 2 H), 4.95−5.15 (m, 1 H), 5.93−6.08 (m, 1 H), 6.18-6.43 (m, 1 H), 6.87 (d, *J* = 7.0 Hz, 1 H), 6.92−7.05 (m, 1 H), 7.15−7.55 (m, 15 H), 8.0 (d, *J* = 7.0 Hz, 1 H), 8.92 (br s, 1 H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 25.04, 65.21, 86.84, 87.61, 92.00, 96.77, 127.42, 127.68, 128.34, 129.04, 133.71, 143.78, 145.70, 155.80, 163.30, 171.03 (several signals of the trityl group overlap); exact mass *m*/*z* calcd for $C_{19}H_{15}$ (M − $C_{11}H_{12}N_3O_4$) 243.1174, found 243.1173; exact mass *m*/*z* calcd for $C_{11}H_{12}N_3O_4$ (M − $C_{19}H_{15}$) 250.0828, found 250.0836.

(b) Use of Na_2Te. Na_2Te (680 mg, 0.393 mmol) (prepared from the elements, as described above) and a small stirring bar were placed in a dry round-bottomed flask fused onto a reflux condenser. The flask was closed with a septum and flushed with Ar. *N*-Acetyl-5′-*O*-(triphenylmethyl)cytidine 2′,3′-bis(methanesulfonate) (107 mg, 0.157 mmol) in THF (2 mL) was then injected, and the mixture was stirred for 24 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 25 cm), using 5:3:2 MeCN−CH_2Cl_2−PhMe, gave **12a** (33 mg, 42%) as a colorless oil, spectroscopically identical to an authentic sample.

***N*-Acetyl-2′,3′-dideoxy-5′-*O*-(triphenylmethyl)cytidine by Hydrogenation of 12a.** *N*-Acetyl-2′,3′-didehydro-2′,3′-dideoxy-5′-*O*-(triphenylmethyl)cytidine (**12a**) (50 mg, 0.101 mmol), EtOAc (3 mL), and MeOH (1 mL) were placed in a test tube together with Pd/charcoal (10% w/w, 10 mg). The test tube was supported with glass wool in a Parr vessel and

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(51) Watanabe, K. A.; Fox, J. J. *Angew. Chem.* **1966**, *78*, 589.

shaken with hydrogen (50 psi) for 4 h. The mixture was filtered and evaporated. Flash chromatography of the residue over silica gel (1 × 30 cm), using 5:3:2 MeCN−CH_2Cl_2−PhMe, gave *N*-acetyl-2′,3′-dideoxy-5′-*O*-(triphenylmethyl)cytidine (30 mg, 61%) as a colorless oil: FTIR (CH_2Cl_2, cast) 3229, 2925, 1717, 1663, 1493 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.88−1.98 (m, 2 H), 2.09−2.20 (m, 4 H), 2.41−2.55 (m, 1 H), 3.36 (dd, J = 4.5, 4.5 Hz, 1 H), 3.49 (dd, J = 2.7, 2.7 Hz, 1 H), 4.22−4.32 (m, 1 H), 6.03 (dd, J = 2.0, 2.0 Hz, 1 H), 7.10 (d, J = 7.5 Hz, 1 H), 7.25−7.49 (m, 15 H), 8.31 (d, J = 7.5 Hz, 1 H), 9.12 (br s, 1 H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 25.08 (q′), 25.17 (t′), 38.87 (t′), 64.38 (t′), 82.20 (d′), 87.63 (s′), 88.32 (d′), 95.48 (d′), 127.67 (d′), 128.38 (d′), 129.05 (d′), 144.02 (s′), 145.31 (d′), 155.36 (s′), 162.71 (s′), 170.50 (s′) (several signals of the trityl group overlap); mass (FAB) m/z calcd for $C_{30}H_{30}N_3O_4$ (M + H) 496.2, found 496.1.

5′-*O*-Acetyluridine 2′,3′-Bis(methanesulfonate) (13). $MeSO_2Cl$ (0.90 mL, 11.60 mmol) in CH_2Cl_2 (1.6 mL) was added dropwise to a stirred and cooled (ice bath) solution of 5′-*O*-acetyluridine[52,53] (332 mg, 1.16 mmol) and pyridine (1.50 mL, 18.5 mmol) in CH_2Cl_2 (3 mL). The ice bath was removed, and stirring was continued for 24 h. The mixture was evaporated at room temperature, and flash chromatography of the residue over silica gel (3.5 × 30 cm), using 3:97 MeOH−CH_2Cl_2, gave, after a second chromatography under the same conditions, **13** (417 mg, 81%): FTIR (MeOH, cast) 1365, 1180 cm^{-1}; ^1H NMR (acetone-d_6, 200 MHz) δ 2.07 (s, 3 H), 3.26 (s, 3 H), 3.32 (s, 3 H), 4.30−4.60 (m, 3 H), 5.48 (t, J = 6.0 Hz, 1 H), 5.55−5.80 (m, 2 H), 6.00 (d, J = 3.0 Hz, 1 H), 7.76 (d, J = 8.0 Hz, 1 H), 10.23 (br s, 1 H); ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 20.61, 38.66, 38.74, 62.58, 75.14, 78.61, 80.24, 91.11, 103.34, 141.93, 151.33, 163.36, 170.57; mass (HRFAB) m/z calcd for ($C_{13}H_{18}N_2O_{11}S_2$ + H) 443.0431, found 443.0398.

5′-*O*-Acetyl-2′,3′-didehydro-2′,3′-dideoxyuridine (13a) from Dimesylate 13. The general procedure was followed, using Te powder (200 mesh, 61 mg, 0.475 mmol), Et_3BHLi (1 M in THF, 1.17 mL, 1.17 mmol), dimesylate **13** (100 mg, 0.226 mmol) in THF (3 mL), and a reaction time of 96 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 30 cm), using 3:97 MeOH−CH_2Cl_2, gave **13a** (7.7 mg, 14%), spectroscopically identical to an authentic[9b,54] sample.

5′-*O*-[(1,1-Dimethylethyl)dimethylsilyl]adenosine 2′,3′-Bis(methanesulfonate) (14). $MeSO_2Cl$ (0.57 mL, 7.3 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a stirred and cooled (0 °C) solution of 5′-*O*-[(1,1-dimethylethyl)dimethylsilyl]adenosine[55] (700 mg, 1.84 mmol) in a mixture of CH_2Cl_2 (2 mL) and pyridine (8.3 mL). After 1 h, the ice bath was removed, and stirring was continued for 24 h; the mixture was then poured onto ice, EtOAc (200 mL) was added, and the organic layer was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 1:19 MeOH−CH_2Cl_2, gave **14** (773 mg, 78%) as a colorless oil: FTIR (CH_2Cl_2, cast) 3315, 3148 cm^{-1}; ^1H NMR (acetone-d_6, 200 MHz) δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.88 (s, 9 H), 3.25 (s, 3 H), 3.32 (s, 3 H), 3.92−4.02 (dd, J = 12.0, 4.0 Hz, 1 H), 4.02−4.15 (dd, J = 12.0, 4.0 Hz, 1 H), 4.38−4.48 (m, 1 H), 5.70−5.80 (apparent t, J = 5.0 Hz, 1 H), 6.08−6.18 (apparent t, J = 5.0 Hz, 1 H), 6.32−6.38 (d, J = 5.0 Hz, 1 H), 6.60−6.76 (br s, 2 H), 8.22 (s, 1 H), 8.25 (s, 1 H); ^{13}C NMR (acetone-d_6, 50.3 MHz) δ −5.40 (two overlapping signals), 18.94, 26.28 (three overlapping signals), 38.67 (two overlapping signals), 62.29, 76.20, 78.31, 83.50, 87.15, 120.89, 140.49, 150.50, 153.96, 157.36; mass (FAB) m/z calcd for $C_{18}H_{32}N_5O_8S_2Si$ (M + H) 538, found 538.

5′-*O*-[(1,1-Dimethylethyl)dimethylsilyl]-2′,3′-didehydro-2′,3′-dideoxyadenosine (14a) from Dimesylate 14. The general procedure was followed, using Te powder (200 mesh, 113 mg, 0.887 mmol), Et_3BHLi (1 M in THF, 2.0 mL, 2.0 mmol), an initial reaction time of *ca.* 6 h, dimesylate **14** (200 mg, 0.372 mmol) in THF (2 mL), and a reaction time of 20 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated at room temperature. Flash chromatography of the residue over silica gel (2 × 15 cm), using 1:19 MeOH−CH_2Cl_2, gave **14a**[56] (101 mg, 78%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3292, 3164, 2927, 1601, 1085, 837 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz) δ 0.04 (s, 3 H), 0.05 (s, 3 H), 0.89 (s, 9 H), 3.82 (d, J = 4.0 Hz, 2 H), 4.94−5.00 (m, 1 H), 5.91 (br s, $W_{1/2}$ = 17 Hz, 2 H), 6.04 (ddd, J = 6.0, 4.0, 2.0 Hz, 1 H), 6.41 (dt J = 6.0, 2.0, 2.0 Hz, 1 H), 7.04−7.08 (m, J = 2.0, 1 H), 8.08 (s, 1 H), 8.30 (s, 1 H); ^{13}C (CD_2Cl_2, 75 MHz) δ −5.17 (q′), −5.06 (q′) (two overlapping signals), 18.95 (s′), 26.29 (q′) (three overlapping signals), 65.45 (t′), 88.27 (d′), 88.68 (d′), 120.19 (s′), 126.06 (d′), 134.96 (d′), 139.81 (d′), 150.44 (s′), 153.58 (d′), 156.01 (s′); exact mass m/z calcd for $C_{16}H_{25}N_5O_2Si$ 347.1778, found 347.1776.

***N*-[(Dimethylamino)methylene]-5′-*O*-[bis(4-methoxyphenyl)phenylmethyl]adenosine 2′,3′-Bis(methanesulfonate) (15).** $MeSO_2Cl$ (0.37 mL, 4.8 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred and cooled (0 °C) solution of *N*-[(dimethylamino)methylene]-5′-*O*-[bis(4-methoxyphenyl)-phenylmethyl]adenosine,[57] (1.001 g, 1.602 mmol), and Et_3N (1.34 mL, 9.61 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred at 0 °C for 30 min, poured onto ice (*ca.* 200 g), and extracted with CH_2Cl_2 (2 × 150 mL). The organic extract was washed with water (1 × 100 mL), saturated aqueous $NaHCO_3$ (1 × 100 mL), and water (1 × 100 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 30 cm), using 49:30:20:1 CH_2Cl_2−PhMe−MeCN−Et_3N, gave **15** (1.089 g, 87%): FTIR (CH_2Cl_2, cast) 1365, 1180 cm^{-1}; ^1H NMR (acetone-d_6, 200 MHz) δ 3.10−3.30 (m, 12 H), 3.40 (dd, J = 11.0, 4.0 Hz, 1 H), 3.62 (dd, J = 11.0, 3.5 Hz, 1 H), 3.75 (s, 3 H), 3.76 (s, 3 H), 4.40−4.60 (m, 1 H), 5.85−6.00 (m, 1 H), 6.30−6.55 (m, 2 H), 6.70−6.90 (m, 4 H), 7.10−7.38 (m, 7 H), 7.38−7.55 (m, 2 H), 8.30 (s, 1 H), 8.31 (s, 1 H), 8.85−9.00 (br s, 1 H); ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 35.02, 38.74, 38.80, 41.13, 55.60 (two overlapping signals), 62.99, 77.08, 77.47, 82.51, 87.67, 87.86, 114.06, 127.68, 128.63, 129.14, 131.04, 136.53, 136.65, 145.76, 152.45, 153.25, 159.14, 159.82, 161.16 (several signals of DMT group overlap); mass (HRFAB) m/z calcd for ($C_{36}H_{40}N_6O_{10}S_2$ + H) 781.2328, found 781.2337.

2′,3′-Didehydro-2′,3′-dideoxy-*N*-[(dimethylamino)-methylene]-5′-*O*-[bis(4-methoxyphenyl)phenylmethyl]-adenosine (15a) from Dimesylate 15. The general procedure was followed, using Te powder (200 mesh, 20 mg, 0.156 mmol), Et_3BHLi (1 M in THF, 0.33 mL, 0.33 mmol), dimesylate **15** (58 mg, 0.074 mmol) in THF (2 mL), and a reaction time of 16 h. The mixture was washed out of the flask with CH_2Cl_2, and evaporated at room temperature. Flash chromatography of the residue over silica gel (1 × 30 cm), using 29:20:50:1 CH_2Cl_2−PhMe−MeCN−Et_3N, gave **15a** (39 mg, *ca.* 89%), containing trace impurities (^1H NMR, 200 MHz): ^1H NMR (acetone-d_6, 200 MHz) δ 3.02−3.30 (m, 6 H), 3.30−3.46 (m, 1 H), 3.46−3.65 (m, 1 H), 3.74 (s, 3 H), 3.75 (s, 3 H), 5.02−5.18 (m, 1 H), 6.15−6.30 (m, 1 H), 6.48−6.60 (m, 1 H), 6.60−6.90 (m, 4 H), 7.00−7.32 (m, 8 H), 7.32−7.50 (m, 2 H), 8.01 (s, 1 H), 8.42 (s, 1 H), 8.86−9.05 (s, 1 H). For characterization the material was processed as described in the next experiment.

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(53) 2′,3′-*O*-Isopropylideneuridine, prepared (91%) by the reported procedure (ref 52), except that the product was isolated by flash chromatography (silica gel, 1:19 MeOH−CH_2Cl_2), had: FTIR (CH_2Cl_2, cast) 3600−3300, 3300−3140, 1692 cm^{-1}; ^1H NMR (acetone-d_6, 200 MHz) δ 1.33 (s, 3 H), 1.53 (s, 3 H), 3.72−3.82 (apparent t, J = 7.6, 3.8 Hz, 2 H), 4.00−4.40 (m, including br s at δ 4.23, 2 H in all), 4.82−5.00 (m, 2 H), 5.55−5.65 (m, 1 H), 5.88−5.95 (d, J = 3.6 Hz, 1 H), 7.85−7.88 (d, J = 8.0 Hz, 1 H), 9.60−10.30 (br s, 1 H); ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 25.57, 27.52, 63.06, 67.97, 80.96, 84.49, 87.43, 95.58, 102.90, 142.96, 150.90, 160.13; exact mass m/z calcd for $C_{12}H_{16}N_2O_6$ 284.1008, found 284.1011. 5′-*O*-Acetyluridine, prepared from 2′,3′-*O*-isopropylideneuridine, had: ^1H NMR (acetone-d_6, 200 MHz) δ 2.08 (s, 3 H), 4.10−4.38 (m, 5 H), 4.38−4.58 (br s, 1 H), 4.60−4.85 (br s, 1 H), 5.60−5.70 (d, J = 8.0 Hz, 1 H), 5.82−5.92 (d, J = 4.0 Hz, 1 H), 7.62−7.72 (d, J = 8.0 Hz, 1 H), 9.75−10.25 (br s, 1 H).

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(55) We thank Dr. G. A. Angoh (Raylo Chemicals) for a gift of this compound. *Cf.* Imbach, J. L.; Gosselin, G. PCT Int. Appl. WO 93 12,128, 24 Jun 1993; *Chem. Abstr.* **1994**, *120*, 135074u.

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5′-*O*-[Bis(4-methoxyphenyl)phenylmethyl]-2′,3′-dideoxyadenosine and Use of *β*-Cyclodextrin for Tellurium Recovery. Te powder (200 mesh, 34 mg, 0.270 mmol) and a small stirring bar were placed in a dry round-bottomed flask fused onto a reflux condenser. The flask was closed with a septum and flushed with Ar. A solution of Et_3BHLi (1 M in THF, 0.60 mL, 0.60 mmol) was injected, and the mixture was stirred at 40 °C for 0.5 h, by which time the mixture had turned white. Dimesylate **15** (100 mg, 0.128 mmol) in THF (2 mL) was added to the resulting Li_2Te suspension. The mixture was stirred at room temperature for 14 h, and then *β*-cyclodextrin (500 mg) was added, together with 5:2.9:2:0.1 MeCN−CH_2Cl_2−PhMe−Et_3N (20 mL). The resulting mixture was evaporated to deposit the Te on the *β*-cyclodextrin and then filtered through a pad of *β*-cyclodextrin (3 × 3 cm), using the above solvent system. Flash chromatography silica gel (1 g) was added to the filtrate, and the mixture was evaporated. MeOH (20 mL) was added, and the mixture was again filtered, using MeOH. The filtrate was evaporated, and MeOH (4 mL) was added, together with Pd/carbon (20 mg). The mixture was placed under H_2 (50 psi) and shaken for 3 h, filtered, and evaporated. At this stage hydrogenation was incomplete (^{1}H NMR). MeOH (4 mL) and Pd/carbon (20 mg) were again added, and the reaction was set up as before and continued for 12 h, at which point hydrogenation was complete (^{1}H NMR). THF (4 mL) and concentrated NH_4OH (0.4 mL) were added, and the mixture was stirred for 1 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 15 cm), using 5:2.9:2:0.1 MeCN−CH_2Cl_2−PhMe-Et_3N, gave 5′-*O*-[bis(4-methoxyphenyl)phenylmethyl]-2′,3′-dideoxyadenosine[58] (30 mg, 43%) as a colorless oil: FTIR (CH_2Cl_2, cast) 3320, 3180 cm^{-1}; ^{1}H NMR (acetone-d_6, 200 MHz) *δ* 2.10−2.35 (m, 2 H), 2.45−2.75 (m, 2 H), 3.22−3.38 (m, 2 H), 3.75 (s, 6 H), 4.28−4.44 (m, 1 H), 6.28−6.38 (m, 1 H), 6.65−6.88 (m, 6 H), 7.10−7.48 (m, 9 H), 8.15 (s, 1 H), 8.19 (s, 1 H); ^{13}C NMR (acetone-d_6, 50.3 MHz) *δ* 27.54, 32.51, 55.52, 66.50, 81.44, 86.07, 86.44, 113.88, 127.48, 128.51, 129.07, 130.92, 137.00 , 146.23, 150.46, 153.50, 157.06, 159.64 (several signals of DMT group overlap); exact mass *m*/*z* calcd for $C_{31}H_{31}N_5O_4$ 537.2376, found 537.2374.

5′-*O*-(4,4-Dimethoxytrityl)inosine 2′,3′-Bis(methanesulfonate) (16). (a) 5′-*O*-(4,4-Dimethoxytrityl)inosine. Pyridine (2 mL) was injected into a stirred solution of inosine (268.2 mg, 1.0 mmol) and 4,4′-dimethoxytrityl chloride (440.5 mg, 1.30 mmol) in dry DMSO (6 mL). Stirring was continued for 12 h. The mixture was poured onto ice and extracted with $CHCl_3$. The combined organic extracts were washed successively with saturated aqueous $NaHCO_3$ (5 mL), water (2 × 10 mL), and brine (5 mL). The organic solution was dried ($MgSO_4$), diluted with PhMe and evaporated (water pump). The residue was taken up in PhMe, and again evaporated. Finally, the residue was kept under oil pump vacuum to remove traces of PhMe. The crude 5′-*O*-protected inosine was used directly in the next step.

(b) 5′-*O*-(4,4-Dimethoxytrityl)inosine 2′,3′-Bis(methanesulfonate) (16). $MeSO_2Cl$ (0.23 mL, 2.97 mmol) in CH_2Cl_2 (3.0 mL) was added dropwise over 20 min to a stirred and cooled (0 °C) solution of 5′-*O*-(4,4-dimethoxytrityl)inosine (432.1 mg, 0.7573 mmol) in pyridine (8 mL). After 10 min, the ice bath was removed, and stirring was continued for 3.5 h. The mixture was poured onto ice (*ca.* 10 g) and extracted with CH_2Cl_2 (100 mL). The organic extract was washed with water (10 mL), aqueous saturated $NaHCO_3$ (2 × 5 mL), water (10 mL), and brine, dried ($MgSO_4$), diluted with PhMe, and evaporated (water pump). Evaporation from PhMe was repeated twice more. Finally, the residue was kept under oil pump vacuum to remove traces of PhMe. Flash chromatography of the residue over silica gel (2.5 × 20 cm), using 90:8:2 $CHCl_3$−MeOH−MeCN, gave **16** (402.2 mg, 59% over two steps) as a colorless oil: FTIR (CH_2Cl_2, cast) 3057, 2934, 1699, 1510, 1367, 1251 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz) *δ* 3.07 (s, 3 H), 3.09 (s, 3 H), 3.41 (dd, *J* = 11.5, 3.8 Hz, 1 H), 3.61 (dd, *J* = 11.5, 3.0 Hz, 1 H), 3.75 (s, 3 H), 3.76 (s, 3 H), 4.48 (dd, *J* = 8.3, 3.5 Hz, 1 H); 5.61 (dd, *J* = 5.5, 5.0 Hz, 1 H), 6.04 (t, *J* = 5.5 Hz, 1 H), 6.23 (d, *J* = 5.5 Hz, 1 H); 6.75−7.50 (m, 13 H), 7.95 (s, 1 H), 8.02 (s, 1 H), 12.25 (s, 1 H); ^{13}C NMR (CD_2Cl_2, 75 MHz) *δ* 38.72 (q′), 55.61 (q′), 62.40 (t′), 76.15 (d′), 77.17 (d′), 82.44 (d′), 86.74 (d′), 87.34 (s′), 113.61 (d′), 126.18 (s′), 127.46 (d′), 128.33 (d′), 128.43 (d′), 130.46 (d′), 135.45 (s′), 135.60 (s′), 144.75 (s′), 158.63 (s′), 159.24 (s′) (the peaks corresponding to carbons 2, 4, and 8 in the purine base were not detected under the experimental conditions employed, and several signals of the DMT group overlap); exact mass *m*/*z* calcd for $C_{21}H_{19}O_2$ (M − $C_{12}H_{15}O_9N_4S_2$) 303.1385, found 303.1383.

(c) 5′-*O*-(4,4-Dimethoxytrityl)-2′,3′-didehydro-2′,3′-dideoxyinosine (16a) from Dimesylate 16. The general procedure was followed, using Te powder (oven dried at 120 °C for 24 h, 200 mesh, 45.1 mg, 0.3534 mmol), Et_3BHLi (1 M in THF, 0.74 mL, 0.74 mmol), an initial reaction time of 1 h at 40 °C, 5′-*O*-(4,4-dimethoxytrityl)inosine 2′,3′-bis(methanesulfonate) (100 mg, 0.138 mmol) in THF (5 mL). The mixture was stirred at 40 °C for 24 h. At this stage all of the dimesylate had reacted (TLC, silica, 7.5:1.8:0.7 CH_2Cl_2−BuOAc−MeOH). The mixture was cooled, washed out of the flask with CH_2Cl_2, and evaporated at room temperature. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using 3:47 MeOH−CH_2Cl_2, gave **16a** (68.8 mg, *ca.* 93%) as an off-white solid containing slight impurities (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2, cast) 3058, 2909, 1703, 1509, 1250 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz) *δ* 3.22 (dd, *J* = 4.0, 4.0 Hz, 1 H), 3.38 (dd, *J* = 6.3, 6.3 Hz, 1 H), 3.8 (s, 6 H), 5.1 (br s, 1 H), 6.09 (d, *J* = 5.8 Hz, 1 H), 6.42 (d, *J* = 6.0 Hz, 1 H), 6.70−6.80 (m, 4 H), 7.05 (br s, $W_{1/2}$ = 6.4 Hz, 1 H), 7.15−7.42 (m, 9 H), 7.85 (s, 1 H), 8.28 (s, 1 H), 12.84 (s, 1 H); ^{13}C NMR (CD_2Cl_2, 100 MHz) *δ* 55.55 (q′), 65.92 (t′), 86.68 (s′), 87.05 (d′), 89.06 (d′), 113.04 (d′), 125.05 (s′), 125.32 (d′), 127.18 (d′), 128.14 (d′), 128.41 (d′), 130.33 (d′), 130.38 (d′), 135.14 (d′), 135.91 (s′), 136.00 (s′), 138.75 (d′), 145.08 (d′), 145.77 (d′), 149.33 (s′), 159.04 (s′), 159.29 (s′) (several signals of DMT group overlap); mass (FAB) *m*/*z* calcd for $C_{31}H_{28}N_4O_5$ (M) 536.2, found 536.3.

5,6-Bis-*O*-(methylsulfonyl)-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (17). $MeSO_2Cl$ (1.82 mL, 23.7 mmol) was added dropwise over 50 min to a stirred and cooled (ice bath) solution of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose[59] (1.11 g, 4.74 mmol) and pyridine (3.10 mL, 37.9 mmol) in CH_2Cl_2. The mixture was stirred at 0 °C for 10 min, and the cold bath was then removed. Stirring was continued for 18 h, and the mixture was poured onto ice (*ca.* 50 g), and extracted with EtOAc (3 × 35 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL), aqueous $CuSO_4$ (10% w/v, 2 × 50 mL), and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (5 × 15 cm), using 7:3 EtOAc−hexane, gave the dimesylate (1.45 g, 78%) as a crystalline solid: mp 78−79 °C; FTIR (CH_2Cl_2, cast) 3000, 1350, 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) *δ* 1.31 (s, 3 H), 1.49 (s, 3 H), 3.06 (s, 3 H), 3.12 (s, 3 H), 3.45 (s, 3 H), 3.85 (d, *J* = 1.8, 1 H), 4.36 (dd, *J* = 9.0, 3.0 Hz, 1 H), 4.44 (dd, *J* = 9.0, 5.4 Hz, 1 H), 4.60 (d, *J* = 3.0 Hz, 1 H), 4.66 (dd, *J* = 9.0, 1.9 Hz, 1 H), 5.16−5.21 (m, 1 H), 5.89 (d, *J* = 3.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) *δ* 26.26 (q′), 26.90 (q′), 37.70 (q′), 39.16 (q′), 57.79 (q′), 68.99 (t′), 74.30 (d′), 77.82 (d′), 80.93 (d′), 82.68 (d′), 105.43 (d′), 112.50 (s′); exact mass *m*/*z* calcd for $C_{11}H_{19}O_{10}S_2$ (M − CH_3) 375.0420, found 375.0419.

5,6-Dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-hex-5-enofuranose (17a) from Dimesylate 17. The general procedure was followed, but with some changes, using Te powder (200 mesh, 187.6 mg, 1.4703 mmol), Et_3BHLi (1 M in THF, 3.8 mL, 3.8 mmol), an initial reaction time of *ca.* 30 min at 75 °C (bath temperature), dimesylate **17** (573.4 mg, 1.4703 mmol) in THF (5 mL) (added at room temperature), and a reaction time of 12 h at room temperature. The mixture was washed out of the flask with Et_2O and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 1:1 EtOAc−hexane, gave **17a** (183 mg, 67%) as a clear oil, identical to an authentic[60] sample.

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(*E*)-3,4-Dideoxy-1,2:5,6-di-*O*-isopropylidene-*erythro*-3(*E*)-hex-3-enitol (18a) from Dimesylate 18. The general procedure was followed, but with minor changes, using Te powder (200 mesh, 191.1 mg, 1.4983 mmol), Et_3BHLi (1 M in THF, 3.9 mL, 3.9 mmol), an initial reaction time of *ca.* 30 min at 70 °C (bath temperature), 1,2:5,6-di-*O*-isopropylidene-3,4-bis-*O*-(methylsulfonyl)-D-glucitol[61] (626.3 mg, 1.4983 mmol) in THF (5 mL) (injected over 2 h at room temperature), and a reaction time of 15 h. The mixture was washed out of the flask with CH_2Cl_2 and evaporated. Flash chromatography of the residue over silica gel (3 × 16 cm), using 3:7 EtOAc−hexane, gave **18a**[24c,62] (254.5 mg, 75%) as a crystalline solid (needles): mp 70−71 °C (lit.[24c,62] mp 69−71 °C).

(±)-2-*exo*-3-*exo*-Camphanediol 2,3-Bis(methanesulfonate) (21). $MeSO_2Cl$ (0.39 mL, 5.0388 mmol) was added over 60 min to a stirred and cooled (ice bath) solution of (±)-2-*exo*-3-*exo*-camphane-2,3-diol[63] (170.0 mg, 1.00 mmol) and pyridine (0.65 mL, 8.0367 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at 0 °C for a further 10 min, the cold bath was removed, and stirring was continued for 5 days, at which point a major product was detected by TLC (silica, 10% EtOAc−CH_2Cl_2). The mixture was poured onto crushed ice (*ca.* 9 g) and washed successively with saturated aqueous $NaHCO_3$ (2 × 10 mL), aqueous $CuSO_4$ (10% w/v, 4 × 10 mL) and brine (10 mL). The organic solution was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 1:9 EtOAc−CH_2Cl_2, gave **21** (233.3 mg, 72%): mp 95−97 °C; FTIR ($CHCl_3$ cast) 2962, 1354, 1175, 1033, 963, 880 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 0.83 (s, 3 H), 1.00 (s, 3 H), 1.10−1.20 (m including s at δ 1.12, 5 H in all), 1.55−1.90 (m, 2 H), 2.12 (d, J = 5.3 Hz, 1 H), 3.09 (s, 6 H), 4.59 (d, J = 7.0 Hz, 1 H), 4.69 (d, J = 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 11.20 (q′), 20.49 (q′), 20.75 (q′), 23.38 (t′), 32.58 (t′), 38.56 (q′), 38.63 (q′), 47.72 (s′), 49.41 (s′), 50.72 (d′), 81.93 (d′), 85.62 (d′); exact mass m/z calcd for $C_{11}H_{18}O_3S$ (M − CH_3SO_3H) 230.0977, found 230.0977.

Methyl 4,6-*O*-Benzylidene-α-D-galactopyranoside 2,3-Bis(methanesulfonate) (22). $MeSO_2Cl$ (0.20 mL, 2.583 mmol) was added over 20 min to a stirred and cooled (0 °C) solution of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside[64] (140.2 mg, 0.497 mmol) and pyridine (0.35 mL, 4.327 mmol) in CH_2Cl_2 (3 mL). After a further 15 min, the ice bath was removed, and stirring was continued for 18 h. The mixture was poured onto crushed ice (*ca.* 5 g) and washed successively with 10% w/v aqueous $CuSO_4$ (until a constant blue color was maintained in the aqueous layer), saturated aqueous $NaHCO_3$ (2 × 10 mL), and brine. The organic extract was dried ($MgSO_4$) and evaporated. The resulting oil was triturated with Et_2O, and the dimesylate (201.1 mg, 92%) was obtained as a crystalline solid: mp 200−202 °C; FTIR (CH_2Cl_2, cast) 3036, 2940, 1173, 1076, 968, 955 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.0 (s, 3 H), 3.27 (s, 3 H), 3.44 (s, 3 H), 3.82−3.96 (m, 2 H), 4.05−4.15 (m, 1 H), 4.28−4.36 (m, 1 H), 4.90−4.95 (m including s at δ 4.94, 2 H in all), 5.05−5.09 (m, 1 H), 5.6 (s, 1 H), 7.35−7.50 (m, 5 H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 38.74 (q′), 38.82 (q′), 55.02 (q′), 64.20 (d′), 68.86 (t′), 75.67 (d′), 76.11 (d′), 78.38 (d′), 100.44 (d′), 102.46 (d′), 126.40 (d′), 128.71 (d′), 129.65 (d′), 137.30 (s′); exact mass m/z calcd. for $C_{16}H_{22}O_{10}S_2$ 438.0654, found 438.0644.

5′-*O*-(Triphenylmethyl)uridine 2′,3′-Cyclic Sulfite (24). $SOCl_2$ (0.06 mL, 0.823 mmol) was added dropwise to a stirred and cooled (0 °C) solution of 5′-*O*-(triphenylmethyl)uridine (221.9 mg, 0.457 mmol) and pyridine (0.09 mL, 1.113 mmol) in CH_2Cl_2 (10 mL). After 15 min, the ice bath was removed, and stirring was continued for 24 h. The mixture was poured onto ice (*ca.* 15 g) and extracted with CH_2Cl_2 (1 × 5 mL). The organic extract was washed with saturated aqueous $CuSO_4$ (1 × 3 mL), saturated aqueous $NaHCO_3$ (1 × 2 mL), water (2 × 1 mL), and brine (1 × 2 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using 1:1 EtOAc−hexane, gave **24** (201.8 mg, 83%) as a colorless oil that consisted of a 2.5:1 mixture of diastereoisomers: FTIR (CH_2Cl_2 cast) 3202, 3060, 1694, 1219, 1003 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ (major isomer only) 3.47 (dd, J = 11.0, 3.5 Hz, 1 H), 3.54 (dd, J = 11.0, 5.0 Hz, 1 H), 4.34 (dd, J = 9.0, 4.0 Hz, 1 H), 5.56 (dd, J = 8.0, 2.0 Hz, 1 H), 5.65 (dd, J = 6.5, 4.0 Hz, 1 H), 5.69 (dd, J = 6.5, 2.5 Hz, 1 H), 5.87 (d, J = 2.5 Hz, 1 H), 7.25−7.50 (m, 16 H), 9.65 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (major isomer only) 63.60 (t′), 84.84 (d′, two overlapping signals), 87.31 (d′), 87.91 (s′), 92.15 (d′), 103.45 (d′), 127.80 (d′), 128.40 (d′), 128.98 (d′), 141.71 (d′), 143.61 (s′), 150.43 (s′), 163.42 (s′); exact mass m/z calcd for $C_{28}H_{24}N_2O_5$ (M − SO_2) 468.1685, found 468.1680.

(6*S*,7*S*)-1,11-Dodecadiene-6,7-diol (26). 4-Bromo-1-butene (678.3 mg, 5.0241 mmol) was added dropwise to a stirred suspension of Mg (174.2 mg, 7.1672 mmol) in Et_2O (2 mL) at such a rate that the mixture refluxed gently. The mixture was refluxed for 30 min after the end of the addition (oil bath at 40 °C) and then allowed to cool. The resulting Grignard reagent[65] was then added dropwise over 5 min by syringe to a stirred and cooled (−30 °C) suspension of anhydrous CuI (66.7 mg, 0.3502 mmol) in THF (5 mL). After a further 5 min, (*S*,*S*)-1,2:3,4-diepoxybutane[66] (115.8 mg, 1.3465 mmol) was added over 15 min. The cold bath was removed and replaced by an ice bath, and stirring was continued for 1.5 h. Saturated aqueous NH_4Cl was then added to the cold suspension, and the mixture was extracted with Et_2O (2 × 10 mL). The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm), using 2:3 EtOAc−hexane, gave **26** (208.1 mg, 91%) as a colorless oil: FTIR (CH_2Cl_2 cast) 3373, 3076, 2996 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.33−1.65 (m, 8 H), 1.98−2.16 (m, 4 H), 2.25 (br s, $W_{1/2}$ = 7.0 Hz, 2 H), 3.32−3.42 (m, 2 H), 4.91−5.07 (m, 4 H), 5.75−5.89 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 25.34, 33.40, 34.06, 74.65, 114.70, 139.18; exact mass m/z calcd for $C_{12}H_{22}O_2$ 198.1620, found 198.1620.

(6*S*,7*S*)-1,11-Dodecadienyl-6,7-diol Bis(methanesulfonate) (27). $MeSO_2Cl$ (0.23 mL, 2.9703 mmol) was added over 15 min to a stirred and cooled (0 °C) solution of **26** (142.1 mg, 0.7177 mmol) and pyridine (0.29 mL, 3.5884 mmol) in CH_2Cl_2 (1.4 mL). The ice bath was removed, and stirring was continued for 6 h. The mixture was poured onto crushed ice (*ca.* 5 g) and washed successively with saturated aqueous $CuSO_4$ (2 × 8 mL), water (10 mL), saturated aqueous $NaHCO_3$ (2 × 10 mL), and brine. The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 3:7 EtOAc−hexane, gave **27** (195.0 mg, 77%) as a yellow oil: FTIR (CH_2Cl_2 cast) 2940, 1356, 1174 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.48−1.59 (m, 4 H), 1.63−1.87 (m, 4 H), 2.02−2.20 (m, 4 H), 3.06 (s, 6 H), 4.72-4.79 (m, 2 H), 4.95−5.07 (m, 4 H), 5.72−5.88 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 24.30 (t′), 29.99 (t′), 33.49 (t′), 39.07 (q′), 81.20 (d′), 115.49 (t′), 138.21 (d′); mass (CI) m/z calcd for $C_{14}H_{26}O_6S_2$ 372.2, found 372.2; exact mass m/z calcd for $C_7H_{12}O_3S$ (M − $C_7H_{14}O_3S$) 176.0507, found 176.0507.

(6*E*)-1,6,11-Dodecatriene (28) from Dimesylate (27). The general procedure was followed, but with minor changes, using Te powder (89.6 mg, 0.7022 mmol), Et_3BHLi (1 M in THF, 1.46 mL, 1.46 mmol), an initial reaction time of *ca.* 60 min at 40 °C (bath temperature), dimesylate **27** (226.2 mg, 0.6381 mmol) in THF (1.3 mL) (added at room temperature), and a reaction time of 2 h. The dark brown suspension was then filtered through a small pad of Celite and evaporated. Kugelrohr distillation (25 °C, 0.1 mmHg) of the resulting yellow liquid gave **28**[67] (99.6 mg, 95%) as a colorless, volatile liquid, containing slight (<4%) impurities (^1H NMR, 300

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MHz): FTIR (CH_2Cl_2 cast) 3076, 2977, 1265 cm^{-1}; ^1H NMR (CD_2Cl_2, 300 MHz) δ 1.38−1.50 (m, 4 H), 1.96−2.10 (m, 8 H), 4.92−5.04 (m, 4 H), 5.39−5.44 (m, 2 H), 5.76−5.90 (m, 2 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 29.34 (t′), 32.43 (t′), 33.64 (t′), 114.49 (t′), 130.74 (d′), 139.42 (d′); exact mass *m*/*z* calcd for $C_{12}H_{20}$ 164.1565, found 164.1568.

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Supporting Information Available: NMR spectra for new compounds that were not analyzed (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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