A New and Convenient Synthesis of 2-Deoxy-D-ribose from 2,4-*O*-Ethylidene-D-erythrose

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A new synthesis is described of 2-deoxy-D-*erythro*-pentose [2-deoxy-D-ribose, 2-deoxy-D-arabinose (1)], starting from D-glucose. The synthesis proceeds through direct olefination of 2,4-*O*-ethylidene-D-erythrose (2) by addition of the stabilized ylides generated from dimethylphosphorylmethyl phenyl sulfide (4) and the corresponding sulfoxide 5. These afford the key intermediates, thio-enol ether 7 and α,β-unsaturated sulfoxide 8, which when subjected to mercuric ion assisted hydrolysis gave high yields of 2-deoxy-D-ribose (1). This facile chain extension of 2 required its existance as a monomer, and conditions effective for obtaining the monomer have been developed. Detailed ^1H and ^{13}C NMR studies of these compounds are presented.

The synthesis of 2-deoxy sugars is an active area of investigation, since these compounds are frequent constituents of biologically important molecules. Specifically, our attention was drawn to the synthesis of 2-deoxy-D-ribose (1), a necessary intermediate in nucleoside synthesis. Previously reported syntheses of 1 appeared unattractive due to relatively poor yields as well as numerous and tedious purifications. The strategies common to essentially all these methods were either a one-carbon degradation of D-glucose[1] or deoxygenation of an appropriately substituted sugar derivative[2] that is less accessible than glucose. An elegant example of the latter strategy is the recent synthesis,[3] which proceeds via the deoxygenation of the pentose arabinose. It occurred to us that a more convenient procedure might be evolved from a two-carbon degradation of glucose with subsequent chain elongation.

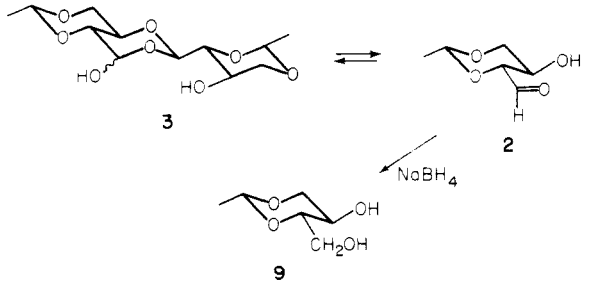
A useful intermediate readily applicable to this approach is 2,4-*O*-ethylidene-D-erythrose (2).[4] However, since it has been reported[5,6] that 2 exists primarily as a dimer 3, its usefulness for chain elongation was in doubt. Thus, for 2 to serve as an efficient intermediate for the synthesis of 1, two questions had to be answered: (1) is it possible to prepare monomer 2; (2) would 2 be amenable to nucleophilic addition and chain elongation via reaction with an ylide in view of the free hydroxyl group, or would an attenuating blocking–deblocking routine be necessary?

Although we were unable to find any reports which unequivocally detail the preparation of monomer 2, a mixture of monomer 2 and dimer 3 has been reported to react with certain nucleophilic reagents under carefully controlled conditions of solvent and temperature. Unfortunately, olefination proceeded in only about 30% yield. The limited nucleophilic additions were rationalized by presuming that some concentration of monomer 2 existed; however, no spectroscopic evidence for monomer formation was presented.[7,8] Despite poor overall yield of olefin, these results are significant, since they illustrate that 2,4-*O*-ethylidene-D-erythrose (2) is a potentially suitable substrate for nucleophilic additions. Its potential rests on the ability to prepare essentially pure monomer and its reaction with an appropriately substituted ylide, which upon hydrolysis would directly afford 1. This report details the successful implementation of this strategy.

Results and Discussion

Preparation of 2,4-*O*-Ethylidene-D-erythrose and Its NMR Evaluation. The synthesis of 2,4-*O*-ethylidene-D-erythrose (2) proceeded via the very efficient periodate degradation of 4,6-*O*-ethylidene-D-glucose (4).[4] Recrystallization of the crude residue afforded crystalline material which exhibited the ^{13}C and ^1H NMR spectra shown in Figures 1 and 2, respectively. No aldehydic resonance appears in either Figure 1 or 2, which is consistent with earlier reports of no aldehydic absorption either in its infrared spectrum[9] or in the ^1H NMR spectrum of its acetates.[7] This lack of aldehydic resonance as well as the complexity of the ^{13}C NMR spectrum leaves no doubt that the product initially isolated is essentially 3.

Presumably, there is an equilibrium between dimer 3



3 2 9

and monomer 2, and one might expect ylide addition to shift the equilibrium as monomer is consumed. However, addition of the ylides generated from either phosphonium salt 6 or phosphonates 4 and 5 did not afford olefin but rather resulted for the most part in the recovery of starting material 3. Although the ethylidene erythrose (2/3) has not previously served as a substrate for the synthesis of 2-deoxy-D-ribose (1), it has been reported[5,6] to afford low yields of olefins upon treatment with certain phosphonate ylides. In a parallel fashion, we also obtained olefins 7 and 8 in poor yield upon treatment of the ethylidene erythrose with the phosphonate ylides 4y and 5y.

In contrast, treatment of crystalline 3 with ethyl acetate containing a catalytic amount of anhydrous acid[10] afforded,

(1) H. W. Diehl and H. G. Fletcher, Jr., *Biochem. Prep.*, 9, 49 (1961).
(2) (a) J. Tomasz, *Acta Chim. Acad. Sci. Hung.*, 70, 263 (1971); (b) R. M. de Lederkremer and L. F. Sola, *Carbohydr. Res.*, 40, 385 (1975).
(3) M. Y. H. Wong and G. R. Gray, *J. Am. Chem. Soc.*, 100, 3548 (1978).
(4) R. Barker and D. L. MacDonald, *J. Am. Chem. Soc.*, 82, 2301 (1960).
(5) H. Paulsen, W. Bartsch, and J. Thiem, *Chem. Ber.*, 104, 2545 (1971).
(6) K. D. Carlson, C. R. Smith, Jr., and I. A. Wolff, *Carbohydr. Res.*, 13, 391, 403 (1970).
(7) Although ref 6 and 8 have ^1H NMR data for the acetates of dimer 3, no ^1H NMR or ^{13}C NMR data for the parent compound were reported.
(8) R. Andersson, O. Theander, and E. Westerlund, *Carbohydr. Res.*, 61, 501 (1978).
(9) R. Schaffer, *J. Am. Chem. Soc.*, 81, 2838 (1959).

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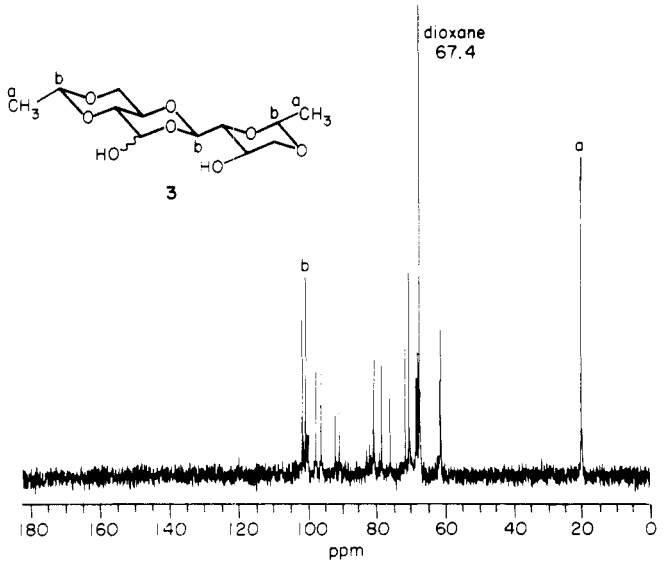


Figure 1. The ^{13}C NMR spectrum of the 2,4-*O*-ethylidene-D-erythrose dimer (**3**).

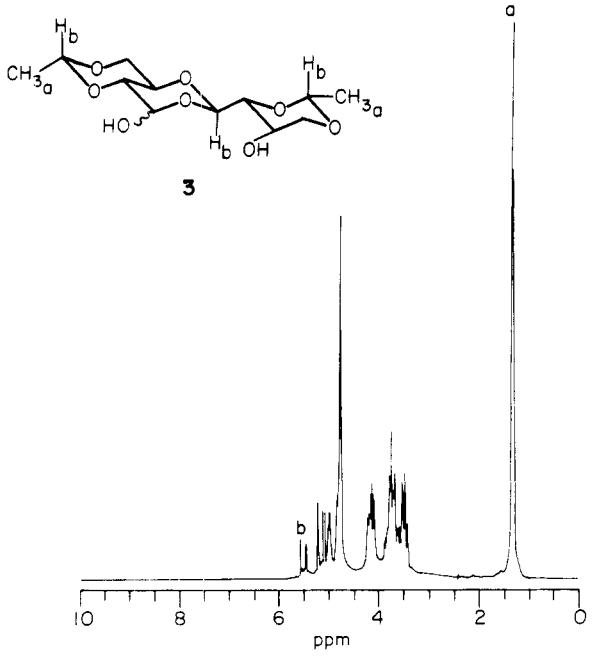


Figure 2. The ^{1}H NMR spectrum of the 2,4-*O*-ethylidene-D-erythrose dimer (**3**) in D_2O (external Me_4Si).

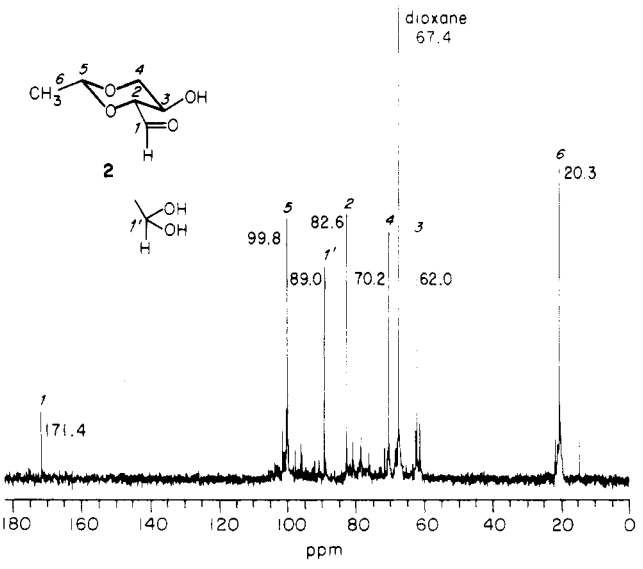


Figure 3. The ^{13}C NMR spectrum of 2,4-*O*-ethylidene-D-erythrose (**2**) resulting from acid–ethyl acetate treatment.

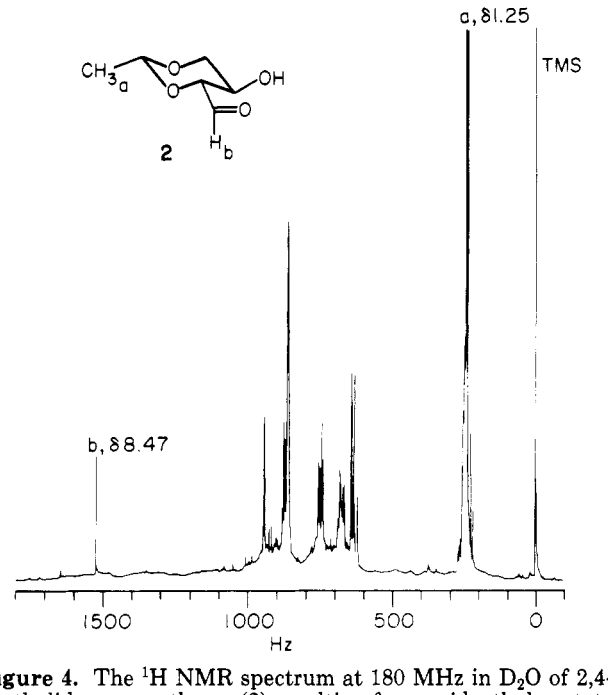


Figure 4. The ^{1}H NMR spectrum at 180 MHz in D_2O of 2,4-*O*-ethylidene-D-erythrose (**2**) resulting from acid–ethyl acetate treatment.

after solvent removal, a solid residue which underwent olefin formation in excellent yield. Thus exposure of **3** to catalytic, anhydrous acid resulted in transformation to the monomeric ethylidene erythrose, **2**.[11] Removal of all traces of acid by continuous azeotropic distillation with either benzene or toluene restored the original dimeric structure, **3**. When this material was then resubmitted to the ylide reaction, it was essentially inactive. Although ylide would be expected to destroy the residual acid and re-established dimer **3**, dimerization under these conditions is much slower than reaction of the ylide with the monomer aldehyde **2**, and high yields of olefins result.

The ^{13}C and ^{1}H NMR spectra of monomeric 2,4-*O*-ethylidene-D-erythrose (**2**) are shown in Figures 3 and 4. The aldehydic resonance now is clearly evident in both spectra. The ^{13}C NMR spectrum is much simpler and indicates that less than 5% of dimer **3** is present. However, it is complicated by an extra absorption, seven carbon resonances appearing instead of the anticipated six. This cannot be due to any diastereomers since such an explanation would result in nonequivalence for more than one carbon resonance. We attempted, therefore, to resolve this apparent anomaly by first reducing **2** with sodium borohydride to the crystalline diol **9**, obtained in 96% yield.[4,6]

The ^{13}C NMR spectrum of diol **9** appears in Figure 5. Along with the lack of an aldehydic resonance, one sees the appearance of the new exocyclic hydroxymethyl absorption at 62.4 ppm. More significant, however, is the absence of the extra resonance which is present in the

(10) Initially anhydrous gaseous hydrochloric acid was used; subsequently we found it much more convenient to use either 100% phosphoric acid or glacial acetic acid.

(11) The possibility that acid might have caused acetal migration was also investigated. Our product **2** is not the 2,3-*O*-ethylidene derivative as shown by direct comparison with authentic 2,3 isomer prepared according to ref 6. Also, since **2** is recovered unchanged from treatment with periodate, it cannot be the 3,4-*O*-ethylidene isomer. Thus the acetal moiety remains unchanged in the acid-catalyzed conversion of **3** to **2** as the 2,4-*O*-ethylidene derivative.

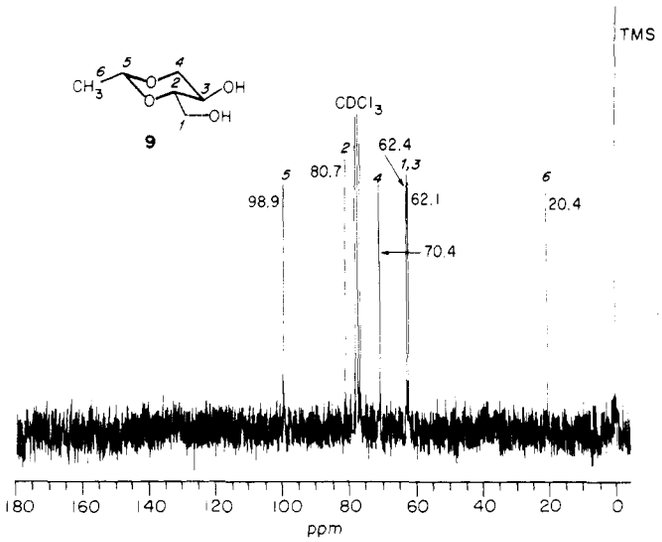


Figure 5. The ^{13}C NMR spectrum of 2,4-*O*-ethylidene-D-erythritol (**9**).

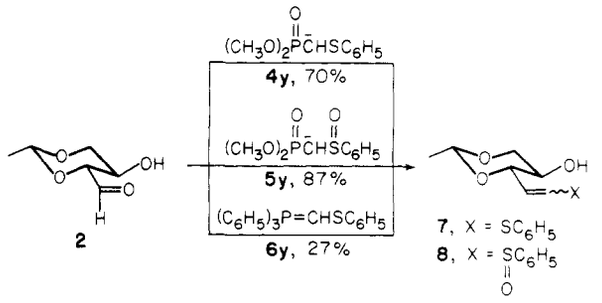
spectrum of **2** (Figure 3). The six signals corresponding to the six carbon nuclei were readily assigned as shown on the basis of chemical shift correlations as well as off-resonance decoupling experiments. On the basis of this spectrum, diol **9** does not evidence nonequivalence; that is, **9** is either diastereomerically pure or, alternatively, the diastereomers have fortuitously coincident chemical shifts. In order to test this latter possibility, we attempted to induce nonequivalence in **9** by incremental addition of a lanthanide shift reagent. When **9** was treated with Eu(fod)$_3$ all diol resonances shifted downfield in both the ^1H and ^{13}C NMR spectra, and there was no induced nonequivalence. Therefore, we conclude that **9** is a single diastereomer which has an equatorial ethylidene methyl. A similar conclusion was reached[6] for 4-*O*-acetyl-1,2-dideoxy-3,5-*O*-ethylidene-1-nitro-D-*erythro*-pent-1-enitol, prepared from **2**. Since **9** is a single diastereomer, **2** must also be diastereomerically pure; therefore, the extra resonance appearing in Figure 3 must arise from another source. Although the spurious resonance may arise from an impurity, this seems unlikely in view of the Eu(fod)$_3$ results; further a dynamic conformational effect may be similarly ruled out.

Examination of the off resonance decoupled ^{13}C NMR spectrum of **3** in D_2O exhibited doublets for all absorptions in the range of 80–100 ppm. It would be reasonable to expect the monomeric material to form a hydrate, and this would account for the absorption appearing at 89 ppm. A ^{13}C NMR spectrum of **2** in dried dioxane did display seven absorptions; however, the resonance at 89 ppm was markedly diminished (<15%) but still present, probably due to residual moisture. This result provides support for the hydrate hypothesis.

Ylide Generation and Olefin Formation. Scheme I outlines the synthesis of 2-deoxy-D-ribose (**1**). The olefination sequence proceeded in moderate to high yield via either the phosphorane **6y** or the phosphonate ylides **4y** and **5y**. The success of the reaction is critically dependent upon the relative basicity of the ylide as well as on the previously described method of preparation of 2,4-*O*-ethylidene-D-erythrose (**2**).

It has been demonstrated[12] that stabilized ylides of type **4y** and **5y** add to a variety of hydroxy-substituted carbonyl substrates to afford either thioenol ethers or α,β-unsaturated sulfoxides. Although stabilized ylides have been applied to the synthesis of sugar moieties, they typically have been used to prepare phosphorylated sugars.[5] One exception, however, is the recent report[13] of the preparation of some deoxyhexoses via the stabilized ylide which was generated from (phenylthiomethyl)triphenylphosphonium chloride (**6**). When applied to **2**, 1 equiv of this ylide, **6y**, afforded olefin **7** in a modest 27% yield; further, the addition of 2 equiv did not significantly improve the yield.

Scheme I. Reaction of 2,4-*O*-Ethylidene-D-erythrose (2) with Various Ylides 4y, 5y, and 6y



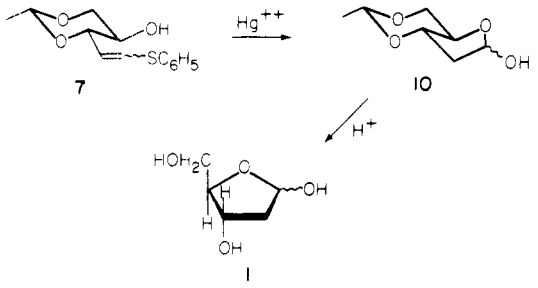
In an effort to improve this yield, we synthesized the stabilized phosphonate ylides **4y** and **5y**. The addition of trimethyl phosphite to α-chloromethyl phenyl sulfide afforded phosphonate **4**, which upon subsequent oxidation with either sodium metaperiodate or peroxybenzoic acid was converted to dimethylphosphorylmethyl phenyl sulfoxide (**5**). Sequential treatment of either **4** or **5** with *n*-butyllithium at −30 and −70 °C, respectively, and then with a dry tetrahydrofuran solution of 2,4-*O*-ethylidene-D-erythrose (**2**) furnished olefins **7** and **8**, typically in 70–90% yields. Although the formation of *E* and *Z* isomers was possible for both **7** and **8**, no effort was made to separate them since any mixture of geometric isomers was suitable for the next step of the synthesis. However, a qualitative assessment of the isomeric (*E*/*Z*) composition was determined by ^1H NMR. Use was made of the established[14,15] coupling constant for the trans vicinal protons in similar systems of 15–16 Hz, whereas the cis vicinal protons evidence a coupling constant of 10–11 Hz. Further, there are well defined chemical shift differences for the *E* and *Z* isomers of similar thioenol ethers[14] as well as α,β-unsaturated sulfoxides.[15] Typically, the proton vicinal to the site of functionality appears at higher field for the *E* isomer of thioenol ethers and at lower field for the *E* isomer of α,β-unsaturated sulfoxides. We noted a similar trend, that is, the chemical shift differences were on the order of 0.20 to 0.40 ppm between the *E* and *Z* isomers, and the respective coupling constants were approximately 15–16 and 10–11 Hz. Utilizing these data as well as the tables of chemical shifts for olefinic substituents,[16] we determined that the *E* isomer was in excess by at least a 2/1 ratio.

Although *n*-butyllithium proved to be a convenient base, we also assayed a variety of other reagents and conditions for ylide generation. For example, there have been several reports[17,18,19] describing the utility of phase transfer cat-

(12) W. S. Wadsworth, Jr., *Org. React.*, **25**, 73 (1977).

(13) H. J. Bestmann and J. Angerer, *Tetrahedron Lett.*, 3665 (1969).
(14) E. J. Cory and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).
(15) M. Mikolajczyk, S. Grzejszczak, and A. Zatorski, *J. Org. Chem.*, 40, 1979 (1975).
(16) (a) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta.*, **49**, 164 (1966); (b) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969).
(17) M. Mikolajczyk, S. Grzejszczak, W. Midura, and A. Zatorski, *Synthesis*, 278 (1975).
(18) E. D'Incan and J. Seyden-Penne, *Synthesis*, 516 (1975).

Scheme II. Conversion of Thioenol Ether 7 to 2-Deoxy-D-ribose (1)



alysts for ylide formation. These were applied in attempted ylide formation from **2**. With a large variety of phase transfer catalysts, ylide formation did not proceed significantly with our substrates. Variations in solvent, temperature, and time as well as base all resulted in essentially no reaction. Also, addition of a mixture of 18-crown-6, either catalytically or stoichiometrically, and potassium *tert*-butoxide in tetrahydrofuran to a tetrahydrofuran solution of phosphonate **4** or **6** and the ethylidene erythrose **2** resulted in no detectable reaction. Finally, alkoxide proved unsatisfactory (<10% yield); however, lithium diisopropylamide at −70 °C, and sodium hydride or potassium hydride, both at −20 °C, all gave satisfactory results. All of these procedures are inferior to ylide generation by addition of *n*-butyllithium to either phosphonates **4** or **5** at −30 and −70 °C, respectively.

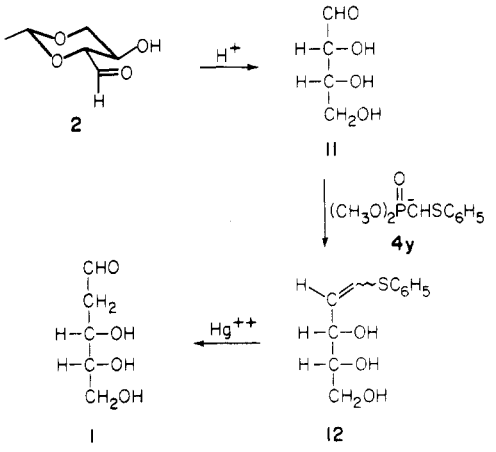
Conversion of Thio-Substituted Olefins to 2-Deoxy-D-ribose (1). All that remained to complete the synthesis of 2-deoxy-D-ribose (**1**) was the hydrolyses of thioenol ether **7** and α,β-unsaturated sulfoxide **8** (Scheme II). We found that treatment of thioenol ether **7** with aqueous sulfuric acid did not afford **1** in satisfactory yields. However, when the hydrolysis was conducted in a stepwise fashion, **1** was obtained in excellent yields. Treatment of **7** first with mercuric chloride in acetonitrile–water, or alternatively with a mercuric oxide–mercuric chloride mixture in acetonitrile–water, afforded, after mild aqueous acid hydrolysis, 2-deoxy-D-ribose (**1**) in greater than 75% yield. The α,β-unsaturated sulfoxide **8** was converted to **1** by exposure to aqueous sulfuric acid; however, this conversion did not proceed as readily as the thioenol ether procedure and afforded **1** in about 30% yield from **8**.

Alternate Synthesis of 2-Deoxy-D-ribose. Since **2**, containing a free hydroxyl group, had been successfully converted into **1**, we considered the possibility of converting D-erythrose (**11**) into **1**. The utility of such an alternate approach stems from the added flexibility of performing the ylide addition in the absence of blocking groups and would provide a model for olefination of underivatized polyhydroxy aldehydes. Thus, hydrolysis of **2** with aqueous sulfuric acid and subsequent treatment with the ylide **4y** generated from dimethylphosphorylmethyl phenyl sulfide (**4**) afforded the triol thioenol ether **12**, which was not isolated but directly treated with a mercuric oxide–mercuric chloride mixture in acetonitrile–water (Scheme III). The resulting crude product was recrystallized from isopropyl alcohol to afford colorless, crystalline **1** in greater than 45% yield.

In summary, we have described a convenient method for the preparation of 2-deoxy-D-ribose (**1**) starting with D-glucose. Our synthesis proceeds via monomeric 2,4-*O*-ethylidene-D-erythrose (**2**) as a key intermediate and affords enhanced overall yields and simplified isolation.

(19) E. V. Dehmlow, *Angew Chem., Int. Ed. Engl.*, **16**, 493 (1977).

Scheme III. Conversion of 2,4-O-Ethylidene-D-erythrose (2) to 2-Deoxy-D-ribose (1) via D-Erythrose (11)



Experimental Section[20]

2,4-*O*-Ethylidene-D-erythrose was prepared from D-glucose via periodate oxidation of 4,6-*O*-ethylidene-D-glucose.[4] Its properties were in agreement with those reported[4-6] and established that the crystallized material was primarily dimer **3** with less than 5% of monomer **2**: ^{1}H NMR (D_2O) δ 1.37 (d, CCH_3), 3.35–3.95 (m, OCH), 4.25 (td, OCH_2), 4.75–5.50 (m, HO and O_2CH); ^{13}C NMR (dioxane) δ 20.13 (CH_3), 61.19 (CHOH, d in the off-resonance spectrum), 67.04, 67.88, 68.32 (CH_2O, t in the off-resonance spectrum), 70.29, 71.50, 75.89, 78.44, 80.59, 90.62, 91.68 (CHO), 95.85, 97.42, 100.23, 101.2 [$HC(CH_3)O_2$]; IR 3435 (OH) cm^{-1}; mp 150–151 °C (lit.[4] mp 149–150 °C); $[\alpha]^{25}_D$ −36.2° (equilibrium, *c* 8.2, H_2O) [lit.[4] $[\alpha]^{20}_D$ −36.8° (equilibrium, *c* 8.25, H_2O)].

The dimer **3**, prepared above, was dissolved in ethyl acetate (20 mL/g), and several drops of glacial acetic acid or 100% phosphoric acid were added.[10] The resulting solution was heated at 90 °C for 20 min, after which it was quickly cooled to 25 °C, and the ethyl acetate was evaporated at this temperature. The solid residue thus obtained was used without further treatment in the olefination reactions. Its properties indicated that it was primarily the monomeric **2,4-*O*-ethylidene-D-erythrose (2)**: ^{1}H NMR (D_2O) δ 1.25 (d, CCH_3), 3.47–3.83 (m, OCH), 4.17 (dd, OCH_2), 4.86–5.28 (m, HO and O_2CH), 8.47 (s, CHO); ^{13}C NMR (dioxane) δ 20.32 (CH_3), 62.09 (CHOH, d in off-resonance spectrum), 70.21 (CH_2O, t in off-resonance spectrum), 82.65 (OCH, d in off-resonance spectrum), 89.0, 99.88 (O_2CH, d in off-resonance spectrum), 171.45 (CHO, d in off-resonance spectrum); IR 3433 (OH), 1718 (C=O) cm^{-1}.

α-Chloromethyl Phenyl Sulfide. A solution of sulfuryl chloride (0.21 mol, 28.4 g) in CH_2Cl_2 was slowly added over a 2-h period to a heated (reflux) solution of methyl phenyl sulfide (0.20 mol, 25 g) in CH_2Cl_2. After addition was complete, the mixture was heated at reflux for another hour and allowed to stand at room temperature overnight. The major portion of the solvent was evaporated and the residue distilled at reduced pressure: yield, 92%; bp 110–115 °C (20 mm) [lit.[21] bp 104 °C (12 mm)]; NMR ($CDCl_3$) δ 4.75 (s, $ClCH_2$), 7.25 (m, C_6H_5).

Dimethylphosphorylmethyl Phenyl Sulfide (4). A mixture of α-chloromethyl phenyl sulfide (41 g, 0.26 mol) and trimethyl phosphite (4 mL/g of sulfide) was heated at 150–160 °C for 36 h. The reaction mixture was allowed to cool to room temperature, and the unreacted trimethyl phosphite was evaporated (40–50 mm) with heating. The residue was then fractionally distilled through a 7-in. Vigreux column at high vacuum to afford a colorless liquid: yield, 83%; bp 140–143 °C (0.5 mm); NMR

(20) All reactions were performed under a nitrogen atmosphere. Solvent evaporations were carried out in vacuo using a Berkeley Rotary Evaporator. All melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM-390, HR-220 or Bruker WH-180. ^{13}C NMR spectra were recorded on a Bruker WH-180; IR spectra were recorded on a Perkin-Elmer 337 spectrophotometer as mulls. CEC-103 and 110B spectrometers were used for determining mass spectra.

(21) F. Bordwell and B. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

($CDCl_3$) δ 3.5 [d, $CH_2P(O)$], 3.71 [d, $(CH_3O)_2P$], 7.29 (multiplet, C_6H_5).

Dimethylphosphorylmethyl Phenyl Sulfoxide (5). To a solution of dimethylphosphorylmethyl phenyl sulfide (**4**, 23.2 g, 0.10 mol) in acetone (130 mL) and water (70 mL), cooled to −5 °C, was added dropwise a solution of sodium metaperiodate (22.5 g, 0.11 mol, in enough water to dissolve the periodate) over 1 h at −5 to 0 °C. The solution was stirred at 0 °C for 4 h and allowed to stand at 5 °C for 24 h, the precipitated sodium iodate was removed, and after evaporation of the acetone, the solution was extracted with $CHCl_3$. Drying over magnesium sulfate and evaporating the $CHCl_3$ gave sulfoxide **5** as a liquid, which was purified by column chromatography on silica, eluting with $CHCl_3/CH_3OH$ 9/1: yield, 95%; NMR ($CDCl_3$) δ 3.29 and 3.5 [AB part of the ABX system, $CH_2P(O)$], 3.72 [overlapping doublets, (CH_3O_2P)], 7.51 (multiplet, C_6H_5).

(Phenylthiomethyl)triphenylphosphonium Chloride (6).[22] To triphenylphosphine (200 g, 0.76 mol) dissolved in benzene (400 mL) was added dropwise α-chloromethyl phenyl sulfide (122 g, 0.78 mol) with stirring at room temperature. After addition was complete, the mixture was heated at reflux with stirring for 10 days. Cooling to room temperature and standing gave the crystalline phosphonium salt **6** in 43% yield: mp 154–156 °C.

Thioenol Ether 7 via Phosphonate 4. To a tetrahydrofuran (12.5 mL) solution of dimethylphosphorylmethyl phenyl sulfide (**4**, 2.32 g, 0.01 mol), cooled to −70 °C, was added over 2 h a hexane solution of *n*-butyllithium (0.011 mol). The mixture was stirred for 1 h at −70 °C and additionally for 2 h at −40 °C, then a tetrahydrofuran (16 mL) solution of 2,4-*O*-ethylidene-D-erythrose (**2**, 2 g, 0.01 mol), prepared as described, was added dropwise to the mixture maintained at −40 °C. After addition was complete, the contents were stirred at −40 °C for 2 h then allowed to slowly warm to room temperature and stirred at room temperature overnight. The residue after evaporation of the solvents was treated with water (25 mL) and extracted with $CHCl_3$ (5 × 15 mL), and the $CHCl_3$ was washed with water (15 mL), dried over magnesium sulfate, and evaporated to afford thioenol ether **7** in 70–75% yield: NMR ($CDCl_3$) δ 1.37 (bd, $CHCH_3$), 3.52–4.31 [$OCHCH(OH)CH_2O$], 4.75 (bqt, CH_3CH), 6.15 (d of d, C_6H_5SCHCH), 6.72 (d, C_6H_5SCHCH), 7.35 (m, C_6H_5); HRMS, calcd. for $C_{13}H_{16}O_3S$ (M^+) 252.0815, found 252.0798.

α,β-Unstaurated Sulfoxide 8. To a dry tetrahydrofuran (20 mL) solution of dimethylphosphorylmethyl phenyl sulfoxide (**5**, 2.48 g, 0.01 mol), cooled to −70 °C, was slowly added over 3 h a hexane solution of *n*-butyllithium (0.011 mol). The mixture was stirred for 4 h at −70 °C, after which a dry tetrahydrofuran (25 mL) solution of 2,4-*O*-ethylidene-D-erythrose (**2**, 2 g, 0.01 mol) was added. After addition was complete, the contents were stirred for 2 h at −70 °C then allowed to slowly warm to room temperature and stirred at room temperature overnight. The reaction mixture was treated exactly as in the isolation of thioenol ether **7** and resulted in a 75–87% yield of α,β-unsaturated sulfoxide **8**: NMR ($CDCl_3$) δ 1.35 (d of d, $CHCH_3$), 3.40–4.25 [m, $OCHCH(OH)CH_2O$], 4.80 (b q, CH_3CH), 6.55 [d, S(O)CH], 7.00 [d of d, S(O)CHCH], 7.55 (m, C_6H_5); HRMS, calcd for $C_{13}H_{16}O_4S$ (M^+) 236.0866, found 236.0861.

Thioenol Ether 7 via Phosphonium Salt 6. To a solution of (phenylthiomethyl)triphenylphosphonium chloride (**6**, 4.20 g, 0.01 mol) in tetrahydrofuran (75 mL), cooled to −25 °C, was added dropwise over 3 h a hexane solution of *n*-butyllithium (0.011 mol). Stirring was continued for 2 h with the temperature maintained at −25 °C, after which a tetrahydrofuran (30 mL) solution of 2,4-*O*-ethylidene-D-erythrose (**2**, 2 g, 0.01 mol) was slowly added over 2 h. The contents were stirred an additional 2 h at −25 °C, allowed to warm to room temperature, and stirred at room temperature overnight. The reaction mixture was treated exactly as above and afforded a 27% yield of thioenol ether **7**, identical with material prepared from phosphonate **4**.

2,4-Ethylidene-D-erythritol (9) was prepared in 96% yield from **3** in a similar fashion to that reported[4,6] for the preparation of **9** from **2**: mp 100 °C (lit. mp 99.5–100.5 °C,[4] 98.5–100.5 °C[6]); $[\alpha]^{22}_D$ −54.3° (*c* 2.0, H_2O) [lit. $[\alpha]^{24}_D$ −54.7° (*c* 2.0, H_2O),[4] $[\alpha]^{25}_D$ −51.1° (*c* 0.67, H_2O)[6]].

2-Deoxy-D-*erythro*-pentose [2-Deoxy-D-ribose (1)]. Procedure A. To a solution of thioenol ether (**7**, 1 g, 3.96 mmol) in acetonitrile/water (3/1, 35 mL) was added a solution of mercuric chloride (2.14 g, 7.92 mmol) in acetonitrile/water (4/1, 35 mL), and the resulting cloudy mixture was stirred at 50 °C for 30 h. The mixture was filtered through Celite, the insoluble portion was washed thoroughly with warm pyridine, and the filtrate was evaporated to a crude residue which was treated with trifluoroacetic acid (0.01 M, 10 mL) at 6 °C for 36 h. The remaining acid was removed by repeated azeotropic distillation with water at reduced pressure, and the residue, upon recrystallization from isopropyl alcohol, afforded colorless, crystalline **1** in 92% yield: mp 92–94 °C (lit. mp 95–98 °C,[1] 96–98 °C[23]); $[\alpha]^{25}_D$ −57.2° (*c* 0.5, H_2O) [lit. $[\alpha]^{20}_D$ −57.6° (*c* 1.1, H_2O),[1] −58° (*c* 1.6, H_2O)[23]]; ^1H and ^{13}C NMR identical with those reported.[3,24]

Procedure B. To a solution of thioenol ether (**7**, 1 g, 3.96 mmol) in acetonitrile/water (4/1, 50 mL) was added with stirring a mixture of yellow mercuric oxide (1.07 g, 3.46 mmol) and mercuric chloride (0.86 g, 3.96 mmol). The contents were heated at 35 °C for 16 h and cooled to room temperature, and the product was isolated exactly as in procedure A. The yield of pure 2-deoxy-D-ribose (**1**) was 88%.

Procedure C via D-Erythrose (11). To a vigorously stirred solution of D-erythrose (**11**, 120 mg, 1 mmol, prepared as described[4]) in DMF (15 mL) or in Me_2SO (15 mL) at −40 °C was added dropwise a THF solution, also at −40 °C, of the ylide **4y** [prepared by the addition of *n*-butyllithium (2 mmol, in hexane) to a THF solution (7 mL) of dimethylphosphorylmethyl phenyl sulfide (**4**, 0.46 g, 2 mmol)]. After addition was completed, the mixture was stirred for 2 h at −40 °C, allowed to warm to 20 °C, and stirred at 20 °C overnight. The mixture was concentrated and treated with mercuric chloride, and the product was isolated as described in procedure A, affording crystalline **1** in 45% yield.

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Registry No. **1**, 533-67-5; **2**, 70377-89-8; **3**, 70369-41-4; **4**, 70369-42-5; **5**, 58496-74-5; **6**, 13884-92-9; (*E*)-**7**, 70369-43-6; (*Z*)-**7**, 70369-44-7; (*E*)-**8**, 70369-45-8; (*Z*)-**8**, 70369-45-8; **9**, 70369-46-9; **11**, 583-50-6; D-glucose, 50-99-7; α-chloromethyl phenyl sulfide, 7205-91-6; methyl phenyl sulfide, 100-68-5; trimethylphosphite, 121-45-9; triphenylphosphine, 603-35-0; 4,6-*O*-ethylidene-D-glucose, 13403-24-2.

(22) Compound **6** has been previously reported (ref 12); however, neither experimental details nor characterizing data were reported.

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