A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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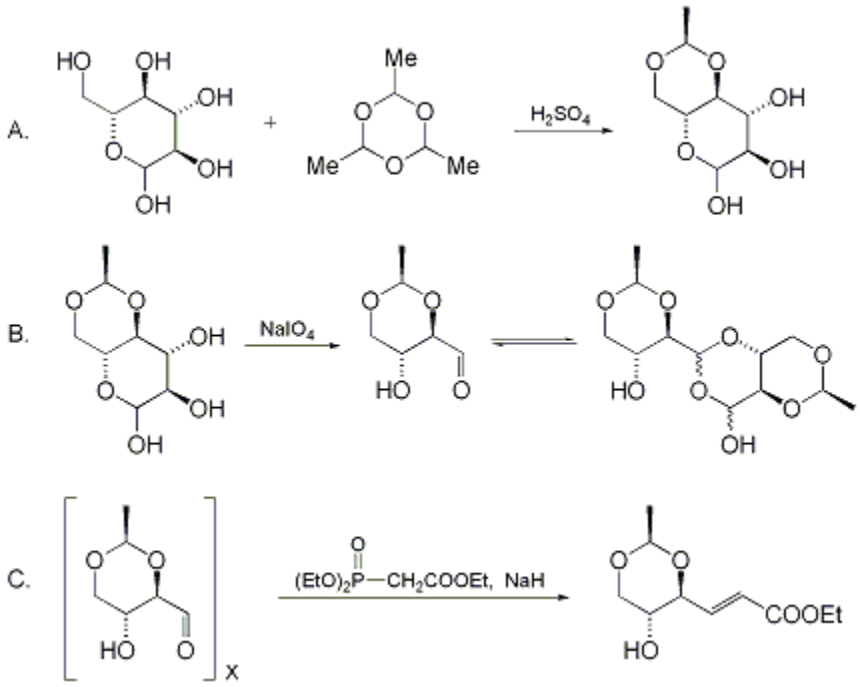
(1'R)-(−)-2,4-O-ETHYLIDENE-D-ERYTHROSE AND ETHYL (E)-(−)-4,6-O-ETHYLIDENE-(4S,5R,1'R)-4,5,6-TRIHYDROXY-2-HEXENOATE

[1,3-Dioxane-(R)-4-carboxaldehyde, 5-hydroxy-2-methyl-, [2R-(2α,4α,5β)]- and D-erythro-Hex-2-enonic acid, 2,3-dideoxy-4,6-O-ethylidene-, ethyl ester [2E,4(S)]-]



Submitted by M. Fengler-Veith, O. Schwardt, U. Kautz, B. Krämer, and V. Jäger[1] .
Checked by Brian Haney, Brian Bucher, and Dennis P. Curran.

1. Procedure

A. (1'R)-(−)-4,6-O-Ethylidene-D-glucose . A 500-mL, round-bottomed flask is charged with D-glucose (81.8 g, 454 mmol, Note 1) and paraldehyde (68.0 g, 514 mmol, Note 2). Concentrated sulfuric acid (0.5 mL) is added dropwise within 30 sec (Note 3) with shaking. The mixture is mechanically shaken for 40 min (Note 4) and then left for 3 days at room temperature. Ethanol (300 mL, Note 5) is added to the adhesive, colorless mass, then the pH is adjusted to 6.5-7 (Note 6) by addition of a 1 N solution of potassium hydroxide in ethanol (Note 7). The residue is dissolved by careful heating. During this procedure the pH is maintained constant by gradual addition of more 1 N ethanolic potassium hydroxide . Charcoal (5 g, Note 8) is added to the yellow solution and the mixture is filtered through a sintered-glass funnel containing a 2-cm pad of Celite. The filter cake is washed with hot ethanol (50 mL). The filtrate, on standing overnight in a freezer at −30°C, deposits a colorless solid material that is recrystallized from ethanol (90 mL) at −30°C (Note 9) to yield 39.4 g (42%) of (−)-4,6-O-ethylidene-D-glucose . The combined mother liquors are concentrated by rotary evaporation (30°C, 30 mm), followed by removal of solvent and excess paraldehyde at room temperature and 0.02 mm (oil vacuum). Recrystallization of the yellowish solid residue from ethanol at −30°C as described above gives another 22.5 g (24%) of product. The combined yield of (1'R)-(−)-4,6-O-ethylidene-D-glucose is 61.9 g (66%), mp 173-174°C (Note 10).

B. (−)-2,4-O-Ethylidene-D-erythrose . A 1-L, three-necked, round-bottomed flask, equipped with a thermometer and two 200-mL pressure-equalizing dropping funnels, is charged with a suspension of sodium metaperiodate (59.2 g, 277 mmol, Note 11) in water (450 mL). The flask is cooled to 0°C using

an ice-water bath. A solution of (−)-4,6-O-ethylidene-D-glucose (29.2 g, 142 mmol, Note 12) in water (120 mL) is added dropwise with stirring and under permanent control of the pH (Note 6) and temperature. The temperature in the flask should be kept below 10°C, and the pH is maintained at approximately 4 by dropwise addition of 8 N aqueous sodium hydroxide (Note 13). After stirring for 3 hr at = 10°C (Note 14), the pH is adjusted to 6.5 by addition of more 8 N sodium hydroxide (Note 15) and stirring is continued for another 2 hr at room temperature. The solution is evaporated under reduced pressure (50°C, 30 mm) and the residue dried at room temperature and 0.02 mm (oil vacuum). To the pale-yellow, solid crude product, ethyl acetate (80 mL) is added and the flask is heated for 2 min at 80° C with stirring. The suspension is filtered and the solid residue is treated three times with ethyl acetate (80 mL each) as described above. The combined, filtered extracts are dried over sodium sulfate for 1 hr with stirring and concentrated by rotary evaporation (30°C, 30 mm), followed by slow (Note 16) removal of solvent at 0.02 mm (oil vacuum) at room temperature to yield 20.1 g (97%) of (−)-2,4-O-ethylidene-D-erythrose as a colorless, amorphous solid, mp 120-121°C (Notes 17, 18).

C. Ethyl (E)-(−)-4,6-O-ethylidene-(4S,5R,1'R)-4,5,6-trihydroxy-2-hexenoate . A 1-L, two-necked, round-bottomed flask, fitted with a nitrogen inlet (Note 19) and a stopper, is oven-dried (140°C) and flushed with nitrogen. The flask is charged with a suspension of sodium hydride in paraffin (6.20 g), containing 60% of sodium hydride (Note 20). The suspension is washed with pentane (3 × 30 mL, Note 21) and the residue is freed from remaining pentane at 0.01 mm (oil vacuum) to give 3.72 g (ca. 155 mmol) of sodium hydride. Under nitrogen, a magnetic stirring bar and tetrahydrofuran (200 mL, Note 22) are added and the flask is sealed with a septum. The suspension is cooled to 0°C and triethyl phosphonoacetate (39.2 g, 175 mmol, Note 23) is added to the stirred sodium hydride / tetrahydrofuran suspension over a period of 5 - 10 min by means of a 100-mL syringe. The mixture is cooled to −78°C (2-propanol/dry ice) and a solution of (−)-2,4-O-ethylidene-D-erythrose (mainly as dimer, 14.6 g, 100 mmol) in tetrahydrofuran (200 mL, Note 22) is added by means of a syringe over 5-10 min. After the mixture is stirred for 15 min at −78°C, it is allowed to warm to room temperature and stirred for another 45 min. The reaction is quenched with saturated ammonium chloride solution (250 mL) and transferred to a 2.5-L separatory funnel with 1200 mL of ether. The aqueous phase is separated and extracted with ether (4 × 100 mL). The combined organic layers are washed with a mixture of saturated sodium bicarbonate/brine (1:1) (2 × 200 mL), dried for 1 hr over magnesium sulfate with stirring, filtered, and evaporated to dryness at 30°C/30 mm to leave 32.0 g of a yellowish oil (Note 24). The crude product is purified by column chromatography over silica (Note 25) with petroleum ether/ethyl acetate 3/2 as eluent (Note 26) to yield 19.2 g of a pale-yellow solid. Recrystallization of the product from n-hexane (Notes 27, 28) affords 15.4 g (71%) of analytically pure ethyl (E)-(−)-4,6-O-ethylidene-4,5,6-trihydroxy-2-hexenoate ; colorless crystals, mp 62-63°C (Notes 29, 30).

2. Notes

1. D-Glucose (BioChemika, = 99.5%) was obtained from Fluka Feinchemikalien GmbH, Neu-Ulm, Germany or Aldrich Chemical Company, Inc.
2. Paraldehyde (= 97%) was obtained from Fluka Feinchemikalien GmbH, Neu-Ulm, Germany or Acros Chemical Company , and was used without distillation.
3. If the sulfuric acid is added too fast, the reaction mixture becomes brown, probably from charring of the glucose.
4. The submitters used a shaking machine (IKA Labortechnik KS 250 basic, ca. 500/min). The checkers used a shaking machine from Lab Line Instruments (Model number 4600).
5. The submitters distilled ethanol (technical grade) from sodium and diethyl phthalate . The checkers used absolute ethyl alcohol from Pharmco .
6. The pH was checked with Merck Universal-Indikatorpapier, range 1-14.
7. Approximately 18 mL of 1 N ethanolic potassium hydroxide was needed.
8. Charcoal (powdered) was obtained from E. Merck KGaA, Darmstadt, Germany or J. T. Baker Chemical Company.
9. The solids are dissolved in hot ethanol and then kept overnight in the freezer at −30°C. The checkers found that standing overnight at −5°C gave similar results.
10. In deuterium oxide (D_2O) the product is a 34/66-mixture of α/β-anomers. The spectral properties of (−)-4,6-O-ethylidene-D-glucose are as follows: ^{1}H NMR (250 MHz, D_2O) δ: 1.22 (d, 3 H, J = 5.0, $CHCH_3$), 3.03-3.78 (m, 5 H, 2-H, 3-H, 4-H, 5-H, 6-H_a), 3.90-4.12 (m, 1 H, 6-H_b), 4.40-5.13 (m, 5 H, 1-

H, 3 OH, $CHCH_3$) ;[2a] $[\alpha]_D^{20}$ −2.3° (H_2O, 2 d, *c* 19.7),[2a] $[\alpha]_D^{20}$ −2.37° (H_2O, equilibrium, *c* 19.7).[3]
11. Sodium periodate ($NaIO_4$) (98%) was obtained from Fluka Feinchemikalien GmbH, Neu-Ulm, Germany or Aldrich Chemical Company, Inc.
12. In several experiments it was found that the yield of 2,4-O-ethylidene-D-erythrose generally is somewhat lower when the reaction is performed on a larger scale.
13. Approximately 24 mL of 8 N sodium hydroxide was used.
14. The pH was checked every 30 min and, if necessary, more aqueous sodium hydroxide was added to keep the pH at 4.
15. Approximately 16 mL of 8 N sodium hydroxide was needed.
16. *Caution: The evaporation of the solvent must be done slowly and carefully because the product shows a strong tendency to foam*.
17. It is difficult to give exact spectral properties of (−)-2,4-O-ethylidene-D-erythrose because of rapid di- and/or oligomerization. The melting points given in the literature differ from 65-80°C[4] to 150-151° C,[5] depending on the degree of oligomerization of the product. With the present procedure, mainly the dimer is obtained. In order to check the optical purity of the product, it is convenient to compare the equilibrium value of specific rotation, as obtained after 2 days in aqueous solution at room temperature: $[\alpha]_D^{20}$ −39.5° (H_2O, 2 d, *c* 1.00),[6] $[\alpha]_D^{20}$ −36.8° (H_2O, equilibrium, *c* 8.25),[3] $[\alpha]_D^{25}$ −36.2° (H_2O, equilibrium, *c* 8.2).[5] The analytical data of the product were as follows:[2a] Calcd for $C_6H_{10}O_4$ (146.14): C, 49.31; H, 6.90. Found: C, 49.18; H, 7.07; ^1H NMR (200.1 MHz, D_2O) δ: 1.38 (d, 3 H, J = 5.0, $CHCH_3$), 3.39-3.99 (m,1 H, OCH), 4.06-4.31 (m, 2 H, OCH_2), 4.75-5.63 (m, 1 H, OH, $CHCH_3$) ; ^{13}C NMR (50.3 MHz, D_2O/dioxane) δ: 20.1 ($CHCH_3$), 61.2 (CHOH), 67.1, 67.9, 68.4 (CH_2O), 70.3, 71.5, 76.0, 78.5, 80.8, 90.6, 91.6 (CHO), 95.6, 97.4, 100.3, 101.2 (O_2CHCH_3) .
18. According to ref. 5, monomeric (−)-2,4-O-ethylidene-D-erythrose may be obtained by heating a solution of the dimer in ethyl acetate with a catalytic amount of glacial acetic acid or 100% phosphoric acid for 20 min at 90°C.
19. Nitrogen was dried by means of a Sicapent(r) (E. Merck) drying tube. The checkers used dry argon.
20. Sodium hydride (60% sodium hydride in paraffin) was obtained from Fluka Feinchemikalien GmbH, Neu-Ulm, Germany or Aldrich Chemical Company, Inc.
21. Pentane (technical grade) was purified by distillation from sodium .
22. Tetrahydrofuran was purified by distillation under nitrogen from a blue solution of sodium and benzophenone .
23. Triethyl phosphonoacetate (Aldrich Chemical Company, Inc.) was purified by distillation (bp 142° C, 10 mm).
24. Crude product contains triethyl phosphonacetate; the isomeric purity (E/Z) of ethyl 4,6-O-ethylidene-(4S,5R,1'R)-4,5,6-trihydroxy-2-hexenoate was > 95 : 5 according to ^{13}C NMR.
25. A 20 cm × 5 cm column packed with 200 g of Kieselgel 60, (E. Merck, 0.040-0.063 mm, 250-400 mesh) was used. The checkers used a 40 cm × 10 cm column packed with silica gel (Bowman Chemical Co., 60Å) and eluted with 1/1 hexane/ethyl acetate with similar results.
26. Ethyl acetate and petroleum ether (technical grade; boiling range 40-80°C) were purified by distillation.
27. Hexane (technical grade) was distilled before use.
28. Hexane was added to the solid in 5-mL portions (ca. 35 mL were needed) until a single phase was formed. On slowly cooling to room temperature, the liquid again separates into two phases before crystallization starts.
29. The analytical data (after chromatography) were as follows:[6] Calcd for $C_{10}H_{16}O_5$ (216.23): C, 55.55; H, 7.46. Found: C, 55.40; H, 7.43. The E/Z ratio was found to be > 99:1 (determined by HPLC): t_E = 4.50 min; t_z = 3.40 min, eluent hexane/ethyl acetate 60/40 [LiChrosorb Si 60 column, E. Merck]. (The Z-diastereomer reference sample was prepared as described in Ref. 7). TLC: R_f = 0.38 (petroleum ether/ethyl acetate 60/40). $[\alpha]_D^{20}$ −41.3° ($CHCl_3$; E/Z > 99:1, *c* 0.500), mp 62-63°C, ref. 7: $[\alpha]_D^{25}$ −35.2° ($CHCl_3$, *c* 1.21), mp 59-60°C. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 14.2 (OCH_2CH_3), 20.4 (O_2CHCH_3), 60.8 (OCH_2CH_3), 65.1 (C-5), 70.7 (C-6), 79.9 (C-4), 98.8 (O_2CHCH_3), 122.2 (C-2), 143.7 (C-3), 166.7 (C-1) ; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, 3 H, J = 7.1, OCH_2CH_3), 1.36 (d, 3 H, J = 5.1, O_2CHCH_3), 2.85 (bs, 1 H, OH), 3.44 (t, 1 H, J = 9.5, 6-H_a), 3.52 (dt, 1 H, J = 4.4, J = 9.5, 5-H), 4.01 (ddd, 1 H, ^4J = 1.7, J = 4.5, J = 9.5, 4-H), 4.14 (dd, 1 H, J = 4.4, J = 9.9, 6-H_b), 4.20 (q, 2 H, J = 7.1, OCH_2CH_3), 4.74 (q, 1 H, J = 5.1, O_2CHCH_3), 6.16 (dd, 1 H, ^4J = 1.7, J = 15.8, 2-H), 7.09 (dd, 1 H, J = 4.5, J = 15.8, 3-H) .

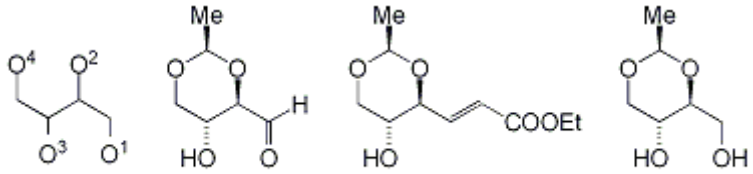
30. In various runs, 20 to 100 mmol of D-erythrose acetal were used, with yields ranging from 65 to 73%.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995 and "Neue Datenblätter für gefährliche Arbeitsstoffe nach der Gefahrstoffverordnung", Welzbacher, U. (Ed.); WEKA Fachverlage, Kissing, 1991.

3. Discussion

Optically active C_4-building blocks of type **1** are versatile starting compounds in organic synthesis. Important members of this class, among numerous others, are derivatives of threose [8,9] and erythrose, respectively, such as 2,4-O-ethylidene-D-erythrose **2**, the corresponding "Horner enoate" **3**, or the erythritol **4**.



1 **2** **3** **4**

As described here, **2** can be prepared in two steps from commercially available D-glucose in up to 65% overall yield. Procedures to obtain the ethylidene glucose[10,11,12] and the ensuing oxidative degradation[3,5,12,13,14,15,16] are based on earlier literature reports. The D-erythrose acetal **2** has also been prepared from D-mannitol in three steps, with an overall yield of 7%.[17] The erythritol **4** can be synthesized from **2** by reduction with sodium borohydride .[3] A mixture of Z/E-**3** (ca. 2 : 1) is known to result from a Witting reaction of **2** with ethoxycarbonylmethylenetriphenylphosphorane .[2a,6,7]

Erythrose derivatives such as **2**-**4**, with a free hydroxy function, offer many possibilities for regioselective conversions; in addition, the free hydroxy group in **2** or **3** does or may influence the regio- and stereoselectivity of additions to the carbonyl group. 2,4-O-Ethylideneerythrose , because of its di- or oligomeric form, is configurationally stable at room temperature and can be stored for several months at room temperature.[9,10,11,12,13,14,15,16,17,18]

Both enantiomers of 2,4-O-ethylideneerythose have been used as intermediates in the preparation of free D- and L-erythrose.[12,13,15,16,17] In some reactions it proved advantageous to promote monomer formation of **2** from the dimer/oligomers by addition of 2-pyridone.[2,19] The N-benzylimine[20] and some hydrazones[20,21] of **2** have been described earlier in the literature. Imines, nitrones, oximes, and nitrile oxides derived from **2** were recently employed in a variety of additions and cycloadditions.[2,22,23] Aldehyde **2** has been transformed in various other Wittig reactions[24,25,26] and in an Abramov reaction with dimethyl phosphite.[27] Formation of the diethyldithioacetal,[28] the dimethyl phosphonate,[29] or the condensation with nitromethane [4,12,30] represent other uses of **2**. 2,3-Epoxyamides were prepared by treating **2** with stabilized sulfur ylides generated in situ.[31] (−)-2,4-O-Ethylidene-D-erythrose **2** has been used for the preparation of 2-deoxy-D-ribose via addition of stabilized ylides and subsequent hydrolysis in the presence of mercuric ion.[5] Further, diastereoselective propargyl addition to the aldehyde **2** was recently performed with propargyl bromide and zinc.[32]

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

(1'R)-(−)-2,4-O-Ethylidene-D-erythrose:
1,3-Dioxane-4-carboxaldehyde, 5-hydroxy-2-methyl-, [2R-(2α,4α,5β)]- (10); (70377-89-8)

Ethyl (E)-(−)-4,6-O-ethylidene-(4S,5R,1'R)-4,5,6-trihydroxy-2-hexenoate:
D-erythro-Hex-2-enonic acid, 2,3-dideoxy-4,6-O-ethylidene-, ethyl ester, Ref. 7: [2E,4(R)]- (12);
(125567-87-5) Ref. 7: [2Z,4(S)]- (12); (125567-86-4)

This prep: [2E,4(S)]- (1'R)-(−)-4,6-O-Ethylidene-D-glucose:
Glucopyranose, 4,6-O-ethylidene- (8);
D-Glucopyranose, 4,6-O-ethylidene- (9); (18465-50-4)

D-Glucose:
α-D-Glucopyranose (8,9); (492-62-6)

Paraldehyde:
s-Trioxane, 2,4,6-trimethyl- (8);
1,3,5-Trioxane, 2,4,6-trimethyl- (9); (123-53-7)

Sodium periodate:
Periodic acid, sodium salt (8,9); (7790-28-5)

Sodium hydride (8,9); (7646-69-7)

Triethyl phosphonoacetate:
Acetic acid, phosphono-, triethyl ester (8);
Acetic acid, (diethoxyphosphinyl)-, ethyl ester (9); (867-13-0)