2,3-*O*-(3-Pentylidene)-D-glyceraldehyde and 2,3-*O*-(3-Pentylidene)-L-glyceraldehyde: Convenient Glyceraldehyde Surrogates Obtained via a Novel Periodate-Based Oxdation System

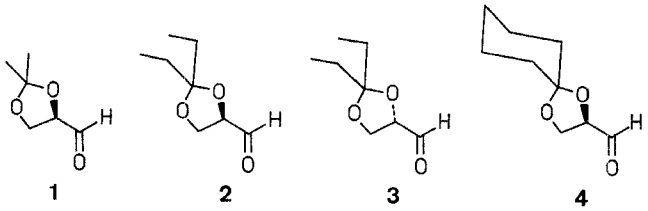
Christopher R. Schmid,* David A. Bradley

Chemical Process Research and Development, Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, IN 46285, USA

Received 4 September 1991

The synthesis of two novel glyceraldehyde surrogates, 2,3-*O*-(3-pentylidene)-D-glyceraldehyde (**2**) and 2,3-*O*-(3-pentylidene)-L-glyceraldehyde (**3**) is presented. Synthesis, handling and storage advantages of **2** and **3** over the conventionally employed 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**) are discussed. The 3-pentanone-derived protecting group facilitates the extraction of product from aqueous oxidation solutions, while the 3-pentanone liberated on ketal deprotection can be efficiently removed at reduced pressures. The synthesis employs a buffered potassium periodate oxidation which offers significant advantages over sodium periodate in glycol cleavage reactions.

We recently required a ketal-protected D-glyceraldehyde as a starting material in multikilogram quantities. Despite our success in implementing a bulk synthesis of 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**),[1] the properties exhibited by the compound severely limit synthesis, processing and storage alternatives. High water solubility prevents efficient extraction of this compound from aqueous media,[2] while the compound's volatility (bp 135°C) limits the use of reduced pressure distillation. Finally, the compound's tendency to polymerize on standing creates handling and storage problems, particularly on multikilogram scale. Prompted by these considerations and poor overall yields (36%), we report here a practical laboratory-scale synthesis of 2,3-*O*-(3-pentylidene)-D-glyceraldehyde (**2**) and an extension of the methodology to the synthesis of 2,3-*O*-(3-pentylidene)-L-glyceraldehyde (**3**). Both compounds are obtained using a novel periodate-based glycol cleavage system, and alleviate the problems associated with **1**.



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

To address the problems associated with **1**, we decided to replaced the isopropylidene ketal with one derived from 3-pentanone. The higher lipophilicity of the resulting protected glyceraldehyde would then enable its extraction from aqueous media, while the higher molecular weight would render it less volatile than **1**. The 3-pentanone (bp 102°C) liberated on deprotection would be easily evaporated.[3] Overall, a wider range of synthesis and processing options would become available.

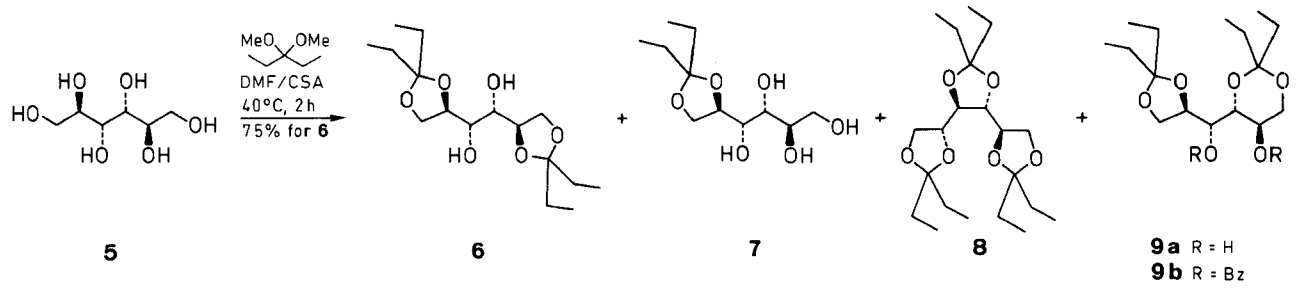
Our approach to **2** took advantage of technology employed in the synthesis of the recently reported cyclohexylidene-protected glyceraldehyde **4**.[3] Thus, D-mannitol (**5**) was ketalized in dimethylformamide (DMF) using 3,3-dimethoxypentane[4] with catalytic camphorsulfonic acid (CSA) to give the 1,2:5,6-diketalized material **6** as the major product. Also detected by ^{1}H NMR was the 1,2-monoketal **7** (1%) and 1,2:3,4:5,6-triketal **8** (5–10%) (Scheme 1). The 1,2:4,6-diketal **9a** (5–7%)[5] was isolated and conclusively identified by the fully decoupled ^{1}H NMR spectrum of its derived benzoate **9b**.

Optimization studies revealed that the highest yield of desired **6** could be obtained at 40°C with 2.1 equivalents of ketalizing reagent. In our hands, recrystallization from a variety of solvents was inefficient; we opted instead to use the crude material after solvent removal. Yields were routinely 70–75% as determined by NMR quantitation against an internal standard.

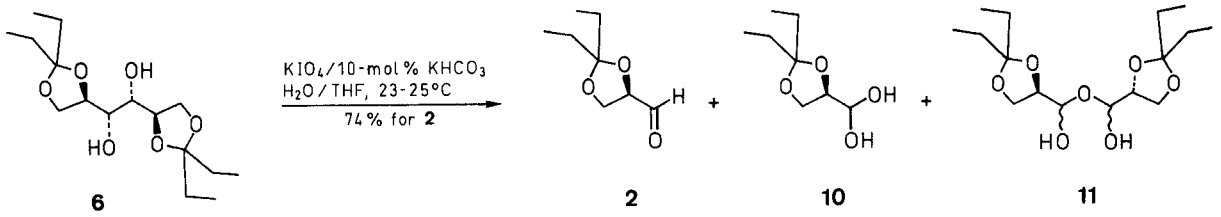
We encountered difficulty employing aqueous sodium periodate ($NaIO_4$) to effect glycol cleavage of **5**. In solution the various hydrated periodates buffered the solution at about pH 3.0-3.5, making pH adjustment difficult.[6] As a result, ketal cleavage was observed under some conditions. Additionally, a strong exotherm required efficient heat removal, even on small scale. We turned to potassium periodate (KIO_4) as an alternative.[7] By virtue of its low aqueous solubility (0.66 g/100 mL at 13°C),[8] it afforded a more desirable solution pH (5–6). Initial experiments gave a slow and incomplete oxidation of **5**. Further, a drop in pH to 3 was observed as a result of formic acid formation from cleavage of monoketal **7**. Surprisingly,[9] oxidations proceeded rapidly and completely with 10 mol-% added potassium hydrogen carbonate ($KHCO_3$), which maintained the solution pH at 7–7.5 throughout the oxidation. These conditions gave complete reaction in 2 hours with no ketal hydrolysis and an easily managed exotherm (Scheme 2).

Examination of the reaction mixture by ^{1}H NMR showed the product to exist predominantly in aqueous solution as the hydrate **10**[10] with some free aldehyde **2** noted; with time, additional hydroxy proton resonances were observed downfield from those due to **10**. We ascribed these resonances to the water-linked dimeric compound **11**, the observed pattern of 4 doublets being consistent with the three diasteromerically distinct combinations possible for **11**. The same resonances for **10** and **11** were observed by NMR when water was added to freshly distilled aldehyde in DMSO-d_6. All three compounds were easily extracted into ethyl acetate from aqueous solution following saturation with sodium chloride. Evaporation of solvent and distillation of the hydrated aldehyde species in vacuo (0.3 mmHg) provided anhydrous **2** in 70–80% yield (ca. 55% from D-mannitol).[11]

For the synthesis of enantiomer **3**, we selected the commercially available ascorbic acid derived[12] starting material L-gulono-1,4-lactone (**12**).[13] Monoketalization of **12** in DMF at room temperature with 3,3-dimeth-

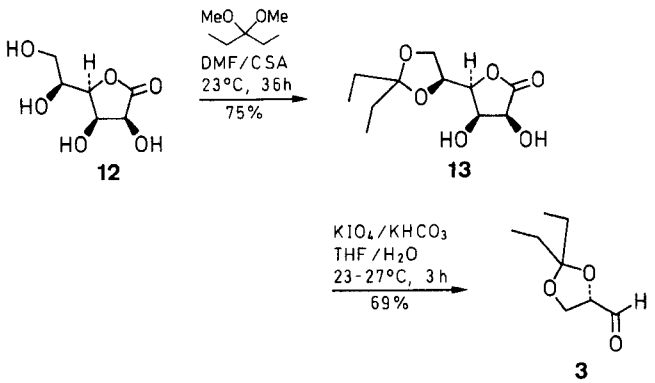


Scheme 1



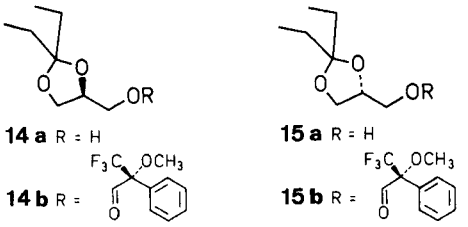
Scheme 2

oxypentane using CSA provided **13** in 73–75% yield (Scheme 3). The resulting lactone was dissolved in tetrahydrofuran (THF) and added dropwise to a slurry of KIO_4 (2.1 equiv) and $KHCO_3$ (2.1 equiv) in water. Gentle evolution of carbon dioxide was observed, as was some mild coloration of the solution, which dissipated as the reaction reached completion. Isolation provided aldehyde **3** in 65–70% yield. Attempts to employ $NaIO_4$ or unbuffered KIO_4, with or without prior lactone opening by aqueous base, led to reagent decomposition as evidenced by substantial coloration of the reaction mixture and decomposition of product upon attempted isolation.[14] The overall yield for the sequence is about 50% from **12**.



Scheme 3

The enantiomeric excess (ee) of the aldehydes was assessed by ^{19}F NMR analysis on the Mosher esters **14b** and **15b** of the corresponding glycerols **14a** and **15a**, obtained from the appropriate aldehyde via sodium borohydride reduction.[15] Values of 99.6% and > 99.7% ee were obtained respectively for **2** and **3**, in good agreement with reports on similar systems by other workers.[16]



Like **1** and **4**, the 3-pentylidene-protected glyceraldehydes **2** and **3** polymerized on standing, evidenced by thickening of the product oil. Redistillation of polymerized material (6–8 mmHg, 70–80 °C), however, provided monomeric aldehyde which retained its stereochemical integrity. Both **2** and **3** (as their corresponding hydrate/dimer/free aldehyde mixture) could be held in ethyl acetate solution once extracted from the aqueous phase; in the case of **2**, no detectable change in chemical or stereochemical potency was observed after 4 weeks storage, and the compound was isolated in 77% yield. The stability and extractability of the dimers and hydrates of **2** and **3** thus provided one solution to the long-standing problem of monomeric stability of this class of compounds.[1,3,12b]

The $KIO_4/KHCO_3$ oxidation system offers obvious advantages over its $NaIO_4$ counterpart for substrates containing acid-sensitive functionality. We are pursuing applications of the system to such areas. Similarly, 3-pentanone-derived ketals can be expected to provide benefits of lipophilicity and low volatility in other situations; other workers have employed them to advantage in different circumstances.[17] For the present case, the 3-pentylidene ketal protecting group confers a set of desirable characteristics on D- and L-glyceraldehyde, which, when combined with the mild KIO_4 oxidation system, enables straightforward synthesis and storage of these chiral pool starting materials.

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, all spectra were obtained in DMSO-d_6. Combustion analyses were performed by Molecular Structure Research at Eli Lilly and Company. Solutions were dried using sodium sulfate followed by filtration except where noted. Removal of volatiles and drying in vacuo were performed at 6–8 mmHg and the temperature as noted.

1,2:5,6-Di-*O*-(3-Pentylidene)-D-Mannitol (6):
To a slurry of D-mannitol **(5)** (25 g, 0.137 mol) in DMF (62.5 mL) containing camphorsulfonic acid (0.96 g) at 40 °C was added 3,3-dimethoxypentane (38 g, 0.288 mol, 2.1 equiv)[4] dropwise over 15 min. Complete solution occurred within 25 min, and the reaction was allowed to proceed for 3 h. Triethylamine (0.7 g) was added and, after transfer to a larger vessel, volatiles were removed *in vacuo* with heating (60 °C) to afford the product as a crude oil containing residual DMF. The oil was diluted with EtOAc (200 mL), washed with half-saturated aqueous NaCl (2 × 135 mL), dried ($MgSO_4$), filtered and the volatiles were again removed with heating (60 °C) to yield a white solid, which was further dried in vacuo overnight at 60 °C to give 43.95 g of material determined to be 75 wt-% **6** (32.96 g, 0.103 mmol, 75%) by quantitation against a measured amount of CH_2Cl_2 by ^1H NMR (32 K data points, 5 s recycle delay between pulses, 30° pulse angle, quantitation against δ 4.65 resonance): mp 94.1–95.3 °C. A portion was recrystallized from EtOAc/hexanes (1:4): mp 97.1–98.1 °C. $[\alpha]_D = +7.8°$ ($c = 5.00$, CH_3OH).

^1H NMR: $\delta = 4.65$ (d, 2 H, $J = 7.8$ Hz), 3.98 (m, 4 H), 3.78 (dd, 2 H, $J = 6.9, 5.3$ Hz), 3.42 (t, 2 H, $J = 7.8$ Hz), 1.47 (m, 8 H), 0.77 (t, 12 H, $J = 7.3$ Hz).

^{13}C NMR: $\delta = 111.97, 74.95, 71.01, 67.57, 29.39, 28.82, 8.11, 7.83$.

IR (KBr): $\nu = 3411, 3295, 2976, 2945, 2883, 1464, 1359, 1273, 1206, 1177, 1088\ cm^{-1}$.

Anal. Calcd for $C_{16}H_{30}O_6$: C, 60.35; H, 9.50. Found: C, 60.56; H, 9.34.

2,3-*O*-(3-Pentylidene)-D-glyceraldehyde (2):
To a slurry of KIO_4 (7.95 g, 34.6 mmol, 1.1 equiv) and $KHCO_3$ (0.32 g, 3.2 mmol, 0.1 equiv) in H_2O (50 mL) at 23 °C (water bath) was added a solution of **6** (13.8 g of 72 wt % material, 10 g, 31.4 mmol) in THF (20 mL) dropwise over 5–10 min, maintaining the temperature of the reaction below 26 °C. The resulting slurry was stirred vigorously for 3 h using a magnetic stir bar, then cooled to 5 °C, and filtered. The filter cake was washed with EtOAc (20 mL) and the washings were added to the aqueous filtrate. The two-phase mixture was then warmed to 23 °C, saturated with NaCl, and filtered again. The layers were then separated, and the aqueous layer was extracted a second time with EtOAc (20 mL). The combined organic layers were dried and volatiles removed in vacuo to afford a viscous syrup, which was transferred to a small distillation vessel, placed under oil pump vacuum (0.3 mmHg) and heated. When material began to appear in the distillation head, chilled fluid (5 °C) was circulated through the condenser, and the receiver was immersed in an ice–water bath. Distillation afforded 7.55 g (47.7 mmol, 76%) of **2** as a clear oil: bp 43–44 °C, 0.3 mmHg; $[\alpha]_D = +80.1°$ ($c = 0.166$, toluene).

^1H NMR: $\delta = 9.57$ (d, 1 H, $J = 1.1$ Hz, H at C-1), 4.46 (m, 1 H), 3.97 (t, 1 H, $J = 8$ Hz), 3.97 (dd, 1 H, $J = 5.1, 8$ Hz), 1.48 (m, 4 H), 0.74 (m, 6 H).

^{13}C NMR: $\delta = 201.36, 114.02, 79.54, 64.79, 28.68, 28.24, 7.83, 7.64$.

IR (neat): $\nu = 2985, 2935, 2880, 1732, 1460, 1200, 1170, 980\ cm^{-1}$.

The product was redistilled (68–72 °C, 6 mmHg) and a portion submitted for analysis: Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.53; H, 8.81.

5,6-*O*-(3-Pentylidene)-L-gulono-1,4-lactone (13):
To a slurry of L-gulono-1,4-lactone **(12)** (Aldrich, 25 g, 140 mmol) in DMF (125 mL) containing camphorsulphonic acid (0.5 g) at 23 °C was added 3,3-dimethoxypentane (33.3 g, 253 mmol, 1.8 equiv) in one portion. The reaction was stirred for 24–48 h, becoming homogeneous. Examination of an aliquot by ^1H NMR at that time showed the reaction to be > 95% complete. Triethylamine (1 mL) was added, the contents were transferred to a larger vessel, and the volatiles were removed in vacuo with heating (60 °C) to afford an oil. A large magnetic stir bar was added to the hot oil, and toluene (375 mL) was rapidly added while vigorous stirring was applied. A precipitate began to form almost immediately. The material was slurried and cooled to 5 °C, vacuum filtered, and the filter cake was rinsed with cold toluene. The material was further dried on the vacuum filter, then in vacuo at 60 °C for 1–3 h to afford 25.93 g (105 mmol, 75%) of **13** as a white solid, containing residual starting material (1–2%) and solvent (< 1%), of sufficient purity for the next step: mp 148.5–149.5 °C. A portion was recrystallized from acetone: mp 149.7–150.8 °C; $[\alpha]_D = +34.4°$ ($c = 0.978$, CH_3OH).

^1H NMR: $\delta = 5.85$ (d, 1 H, $J = 7.4$ Hz), 5.40 (d, 1 H, $J = 4.1$ Hz), 4.39 (dd, 1 H, $J = 4.6, 7.4$ Hz), 4.26–4.12 (m, 3 H), 4.06 (m, 1 H), 3.66 (approx t, 1 H), 1.54 (m, 4 H), 0.78 (m, 6 H).

^{13}C NMR: $\delta = 175.83, 112.75, 81.17, 75.34, 70.11, 69.11, 64.9, 29.05, 28.77, 7.99, 7.75$.

IR (KBr): $\nu = 3449, 2967, 2934, 2882, 1771, 1754, 1219, 1177\ cm^{-1}$.

Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.91; H, 7.50.

2,3-*O*-(3-Pentylidene)-L-glyceraldehyde (3):
To a slurry of KIO_4 (19.65 g, 85.2 mmol, 2.1 equiv) and $KHCO_3$ (8.54 g, 85.4 mmol, 2.1 equiv) in water (50 mL) at 23 °C (water bath cooling) was added a solution of **13** (10.0 g, 40.4 mmol) in THF (50 mL) over 10 min via addition funnel, maintaining the temperature between 23–27 °C. After 3 h, the reaction was chilled to 5 °C, filtered, and EtOAc (25 mL) was added to the filtrate. The two-phase mixture was then warmed to r.t., saturated by addition of solid NaCl, and filtered again. The layers were separated, and the aqueous layer was extracted with additional EtOAc (25 mL). The combined organic layers were dried and the volatiles removed in vacuo. The residual oil was transferred to a distillation apparatus and placed under oil pump vacuum (0.3 mmHg) while gentle heating was applied. When material began to distill, chilled fluid (5 °C) was circulated through the condenser, and the receiving flask was immersed in an ice–water bath. Distillation afforded 4.42 g (27.9 mmol, 69%) of **3** as a clear oil: bp 43–44 °C, 0.3 mmHg); $[\alpha]_D = -79.4°$ ($c = 1.18$, toluene); spectral data as in **2** above.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.58; H, 8.95.

(1) Schmid, C.R.; Bryant, J.D.; Dowlatzadeh, M.; Philips, J.L.; Prather, D.E.; Schantz, R.E.; Sear, N.L.; Vianco, C.S. *J. Org. Chem.* **1991**, *56*, 4056.

(2) Unpublished results (CRS) show 2-butanone to be the most effective common organic solvent for the extraction of **1** into organic solution from saturated aqueous sodium chloride; the compound partitions equally ($K = 1$) between the two phases.

(3) Cyclohexylidene-protected glyceraldehyde **4** behaves similarly to **2** and **3**, but the cyclohexanone liberated on deprotection cannot be conveniently evaporated (bp 152 °C), and must be separated from desired product by other means. For the synthesis of **4**, see:
Sugiyama, T.; Sugawara, H.; Watanabe, M.; Yamashita, K. *Agric. Biol. Chem.* **1984**, *48*, 1841.
For a synthesis of the L-enantiomer, see: Grauert, M.; Schollkopf, U. *Liebigs Ann. Chem.* **1985**, 1817.

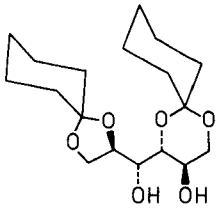
(4) 3-Pentanone (1.1 equiv) was added dropwise over 30 min to 1.0 equiv of trimethyl orthoformate at 5 °C containing 1 wt-% Amberlyst A-15. The cold bath was removed, the reaction warmed to 23 °C and left for 3–5 h until complete, as determined by ^1H NMR. The solids were vacuum filtered through Hyflo, and the filtrate distilled at 6–8 mmHg (evaporation of methyl formate) into a chilled receiver to separate acidic residues. It was then fractionated at atmospheric pressure through a 10″ vigreux column, collecting the fraction distilling above 125 °C to give 80–90% yield of 3,3-dimethoxypentane.

This procedure modifies that of: Huggins, M.J.; Kubler, D.G. *J. Org. Chem.* **1975**, *40*, 2813. Attempts to ketalize D-mannitol directly using 3-pentanone and trimethyl orthoformate (cf. ref. 3) were unsuccessful, affording a complex mixture.

(5) Data for **9a**: ^{1}H NMR: δ = 4.79 (d, 1 H, J = 5.2 Hz), 4.46 (d, 1 H, J = 8 Hz), 3.96 (m, 2 H), 3.63 (m, 5 H), 3.45 (m, 1 H), 1.93 (m, 1 H), 1.48 (m, 7 H), 0.77 (m, 12 H).
^{13}C NMR: δ = 111.81, 100.76, 74.70, 72.51, 69.05, 67.78, 63.94, 60.63, 29.61, 29.37, 29.00, 20.78, 7.99, 7.88, 7.63, 7.24. IR ($CHCl_3$): ν = 3435, 3020, 2978, 2943, 2885, 1464, 1360, 1080, 917 cm^{-1}.

Anal. Calcd for $C_{16}H_{30}O_6$: C, 60.35; H, 9.50. Found: C, 60.54; H, 9.76.

The analogous 1,2:4,6-dicyclohexylidene-D-mannitol **16** has been reported.[3]



16

(6) L.F. Fieser and M.L. Fieser, *Reagents for Organic Synthesis*, New York: Wiley-Interscience, 1972, Vol. I, p. 815 states that pK_{a_2} = 5.7 for periodic acid; a saturated solution (0.58 M) of $NaIO_4$ would give a solution pH of 2.9.

(7) A literature search uncovered only 7 references for the use of KIO_4 in glycol cleavage chemistry:
Ohle, H. *Chem. Ber.* **1943**, *76*, 624.
Weygand, F.; Wacker, A.; Schmeid-Kowarzik, V. *Chem. Ber.* **1949**, *82*, 25.
Mitchell, D.L. *Can. J. Chem.* **1963**, *41*, 214.
Hyman, J.R.; Schmid, H. *Helv. Chim. Acta.* **1966**, *49*, 2067.
Saeki, H.; Shimada, Y.; Kawakita, N.; Shimizu, B.; Ohki, Eiji; Maeda, K.; Umezawa, H. *Chem. Pharm. Bull.* **1973**, *21*, 163–170.
Kalsi, P.S.; Kaur, P.P.; Singh, J.; Chhabra, B. *Chem. Ind.* **1987**, *11*, 394–395.
Yamauchi, K.; Une, F.; Tabata, S.; Kinoshita, M. *J. Chem. Soc., Perk. Trans. 1*, **1986**, 765.

(8) *Handbook of Chemistry and Physics* Weast, R.C., Ed., 57th edition. Cleveland, OH: CRC Press, 1977, p. B-146.

(9) Solutions of $NaIO_4$ rapidly precipitate the highly insoluble para-periodate $Na_2H_3IO_6$ upon addition of NaOH; however, the situation appears to be reversed for KIO_4 with KOH, where the para-periodate $K_2H_3IO_6$ is more soluble than KIO_4. See: Hill, A.E. *J. Am. Chem. Soc.* **1928**, *50*, 2678. We assume that hydrated KIO_4 also functions as a buffer whose solubility-limited capacity is overwhelmed by bicarbonate; oxidation at pH 7–7.5 suggests that the oxidant is actually $K_2H_3IO_6$ or some equivalent hydrated dianionic periodate species.

(10) In situ spectroscopic data for **10**: ^{1}H NMR: δ = 5.89 (d, 1 H, J = 6 Hz), 5.87 (d, 1 H, J = 6 Hz), 4.57 (q, 1 H, 6 Hz), 3.87 (t, 1 H, J = 6 Hz), 3.74 (q, 1 H, J = 6 Hz), 3.60 (t, 1 H, J = 6 Hz), 1.48 (m, 4 H), 0.76 (m, 6 H).
^{13}C NMR: δ = 112.7, 104.9, 91.4, 79.6, 66.6, 29.6, 29.3, 8.5, 8.3.

(11) The distillation served to liberate water of hydration, which was efficiently volatilized at oil pump (0.3 mmHg) pressures. Atmospheric distillation of solvent, followed by distillation of product at 6–8 mmHg also provided the anhydrous aldehyde, but was accompanied by small amounts (1–1.5%) of enantiomeric aldehyde from racemization which we were unable to suppress. Conventional dessicants such as magnesium or sodium sulfate failed to dehydrate the aldehyde.

(12) Hubschwerlen, C. *Synthesis* **1986**, 962.
Jung, M.E.; Shaw, T.J. *J. Am. Chem. Soc.* **1980**, *102*, 6304.
Mikkilineni, A.B.; Kumar, P.; Abushanab, E. *J. Org. Chem.* **1988**, *53*, 6005.
For additional references see: DeWilde, H.; DeClercq, P.; Vandewalle, M. *Tetrahedron Lett.* **1987**, *28*, 4757.

(13) Andrews, G.C.; Crawford, T.C.; Bacon, B.E. *J. Org. Chem.* **1981**, *46*, 2976.

(14) Portionwise sequential addition of $NaIO_4$ followed by NaOH (to pH 5) at 0 °C has been employed in this class of substrates to effect oxidation, but was unattractive to us as a potential large scale procedure.[12a]

(15) Dale, J.A.; Dull, D.L.; Mosher, H.S. *J. Org. Chem.* **1969**, *34*, 2543. We substituted a catalytic amount of DMF for NaCl in the preparation of this acid chloride and obtained complete and clean reaction within 16 h. Glycerols **14a** and **15a** were derivatized using 1.5 equiv each of the *S*-(+) Mosher acid chloride (> 99.6% ee) and pyridine in dichloromethane (2 mL) on a 40 mg scale. The glycerols were obtained by reduction of either **2** or **3** in 1:1 H_2O:MeOH at 5 °C with 4 equiv $NaBH_4$ for 1 h, followed by quench with acetone. Analysis by ^{19}F NMR was performed on the crude product so obtained.

(16) Hirth, G.; Walther, W. *Helv. Chim. Acta* **1985**, *68*, 1863.

(17) Masamune, S.; Ma, P.; Okumoto, H.; Ellingboe, J.W.; Ito, Y. *J. Org. Chem.* **1984**, *49*, 2834.
Hanessian, S.; Sahoo, S.P.; Murray, P.J. *Tetrahedron Lett.* **1985**, *26*, 5631.
Hanessian, S.; Hodges, P.J.; Murray, P.J.; Sahoo, S.P. *J. Chem. Soc., Chem. Commun.* **1986**, 754.
Hanessian, S.; Sahoo, S.; Botta, M. *Tetrahedron Lett.* **1987**, *28*, 1147.
Kim, B.M.; Sharpless, K.B. *Tetrahedron Lett.* **1989**, *30*, 655.