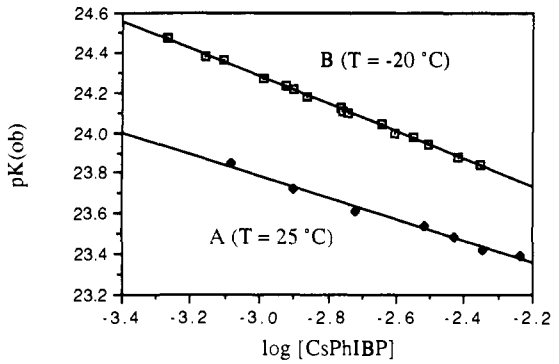


Figure 1. Dependence of the observed cesium ion pair acidity of PhIBP on the concentration of Cs-PhIBP. The slope of the plot is equal to $1/\bar{n} - 1$, where $\bar{n}$ is the average equilibrium aggregation number[8] of Cs-PhIBP. A: $T = 25$ °C, slope = -0.54 ± 0.03. B: $T = -20$ °C, slope = -0.69 ± 0.02.

Table I. Initial Rate Kinetics for the Reaction of Cs-PhIBP with MeOTs in THF[a]

T (°C)	log k	x^b	y^c	$\bar{n}_k{}^d$
25.0[e]	-2.3 ± 0.3	0.23 ± 0.05	1.02 ± 0.07	0.50 ± 0.11
-20.0[f]	-4.0 ± 0.1	0.22 ± 0.02	1.16 ± 0.04	0.70 ± 0.07

[a] Errors are 1 standard deviation. [b] Kinetic order in Cs-PhIBP. [c] Kinetic order in MeOTs. [d] Kinetic aggregation number. See text. [e] Twelve points. [f] Eighteen points.

number and $\bar{n}_k$, the average "kinetic aggregation number", is the average aggregation number over those aggregates that react directly with the electrophile. The results are summarized in Table I. The fractional orders in Cs-PhIBP indicate that aggregates lower than those predominating at equilibrium are the actual reactive intermediates. A value of $\bar{n}_k = 0.5$ means that a dissociated species is the reactive entity; that is, at 25 °C we find that the reactive species is the free enolate ion, even though Cs-PhIBP is substantially aggregated![12] Since these ion pairs are more tightly bound than the monomeric indicator cesium salts, conductivity studies of the indicators[13] then indicate that the free enolate ion is present at no higher than about 5×10^{-6} M when the total enolate concentration is 2.5×10^{-3} M; therefore, the free enolate ion must be at least about 1000 times as reactive toward MeOTs as the predominating aggregate(s). At −20 °C the identity of the reactive intermediate(s) is somewhat ambiguous ($\bar{n}_k = 0.70$), but it is clear that the free enolate ion still plays an important role in the reaction.

Products of the reaction were analyzed by gas chromatography. The ratio of products resulting from alkylation at carbon to those resulting from alkylation at oxygen (the C/O ratio) is about 1.2, independent of the temperature and the extent of reaction. The insensitivity of the product distribution to the extent of conversion is evidence that the CsOTs does not affect $\bar{n}_k$; that is, the free enolate ion is the reactive intermediate throughout the reaction. That the C/O ratio is insensitive to the temperature is surprising, given that $\bar{n}_k = 0.70$ at −20 °C; that is, at this temperature, species other than the free enolate ion (monomeric ion pair or higher aggregates) apparently contribute significantly to the reactivity. However, it is possible to show that any mechanism that changes the free ion concentration ratio $[PhIBP^-]/[Cs^+]$ to a value greater than unity will cause an increase in the value of $\bar{n}_k$, even if the free enolate ion is the only reactive intermediate. For example, this effect would occur if CsOTs or Cs-PhIBP aggregates complexed a fraction of the free Cs^+.

Finally, in a preliminary experiment, the lithium enolate of PhIBP was treated with MeOTs in THF at 25 °C. The reaction was slow compared to the Cs-PhIBP reactions, and after about 10% reaction, the C/O ratio was about 0.4. This result establishes that the free enolate ion is not the dominant reactive intermediate in this case (compared to the C/O ratio obtained in the Cs-PhIBP reactions). Moreover, the lithium cation apparently diminishes the nucleophilicity of the carbon atom relative to the oxygen.

Acknowledgment. This research was supported in part by NIH Grant GM 33609.

(12) The importance of free ions in the reactivity of other highly aggregated systems has been shown in ref 4a. In other instances where free ions have been shown to be reactive intermediates, the systems are aggregated only up to the monomeric ion pair. See, for example, refs 4b and 4c.

(13) Kaufman, M. J.; Gronert, S.; Streitwieser, A. *J. Am. Chem. Soc.* **1988**, *110*, 2829-35.

β-Sialyl Phosphite and Phosphoramidite: Synthesis and Application to the Chemoenzymatic Synthesis of CMP-Sialic Acid and Sialyl Oligosaccharides

Hirosato Kondo,† Yoshitaka Ichikawa, and Chi-Huey Wong*

Department of Chemistry, The Scripps Research Institute, 10666 North Torrey Pines Road La Jolla, California 92037

Received July 28, 1992

A major problem in oligosaccharide synthesis[1] is sialylation.[2] The tertially hindered anomeric center and the lack of an electron-demanding group adjacent to the anomeric center of sialic acid (NeuAc) make the sialylation reaction particularly difficult to execute in an elimination-free and stereocontrolled manner. The same problems are also encountered in the chemical synthesis of CMP-NeuAc. Here we report the synthesis of β-sialyl dibenzyl phosphite using dibenzyl *N,N*-diethylphosphoramidite[3] (DDP) and the application of the glycosyl phosphite[4] to the synthesis of α2,6- and α2,3-linked sialyl saccharides. We also report the chemical synthesis of a protected CMP-sialic acid for use in the study of enzymatic transfer of unnatural NeuAc.[5]

† On leave from the Pharmaceutical Division, Kanebo, Ltd., Osaka, Japan.

(1) For representative chemical glycosylation: (a) Lemieux, R. U. *Chem. Soc. Rev.* **1978**, *7*, 423. (b) Paulson, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. (c) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212. (d) Kunz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 294. (e) Okamoto, K.; Goto, T. *Tetrahedron* **1989**, *45*, 5835. (f) Nicolaou, K. C.; Caufield, T.; Kataoka, H.; Kumazawa, T. *J. Am. Chem. Soc.* **1988**, *110*, 7910. (g) Mootoo, D. R.; Konradsson, P.; Udodong, U.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 5583. (h) Halcomb, R. L.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6661. (i) Friesen, R. W.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6656. (j) Barrett, A. G. M.; Bezuidenhoudt, B. C. B.; Gasiecki, A. F.; Howell, A. R.; Russell, M. A. *J. Am. Chem. Soc.* **1989**, *111*, 1392. (k) Briner, K.; Vesella, A. *Helv. Chim. Acta* **1989**, *72*, 1371. (l) Kahne, D.; Walker, S.; Cheng, Y.; Van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 6881. (m) Suzuki, K.; Maeta, H.; Matsumoto, T. *Tetrahedron Lett.* **1989**, *36*, 4853. (n) DeNinno, M. P. *Synthesis* **1991**, 583. For reviews of enzymatic glycosylation: (o) Ichikawa, Y.; Look, G. C.; Wong, C.-H. *Anal. Biochem.* **1992**, *202*, 215. (p) Drueckhammer, D. G.; Hennen, W. J.; Pederson, R. L.; Barbas, C. F.; Gautheron, C. M.; Krach, T.; Wong, C.-H. *Synthesis* **1991**, *7*, 499. (q) Toone, E. J.; Simon, E. S.; Bednarski, M. D.; Whitesides, G. M. *Tetrahedron* **1989**, *45*, 5365. (r) David, S.; Auge, C.; Gautheron, C. *Adv. Carbohydr. Chem.* **1991**, *49*, 175.

(2) (a) Ito, Y.; Ogawa, T. *Tetrahedron* **1990**, *46*, 89. (b) Hasegawa, A.; Nagahama, T.; Ohki, H.; Hotta, H.; Kiso, M. *J. Carbohydr. Chem.* **1991**, *10*, 493. (c) Marra, A.; Sinay, P. *Carbohydr. Res.* **1990**, *195*, 303. (d) Lonn, H.; Stenvall, K. *Tetrahedron Lett.* **1992**, *33*, 115. (e) Kirchner, E.; Thiem, F.; Dernick, R.; Heukeshoven, J.; Thiem, J. *J. Carbohydr. Chem.* **1988**, *7*, 453.

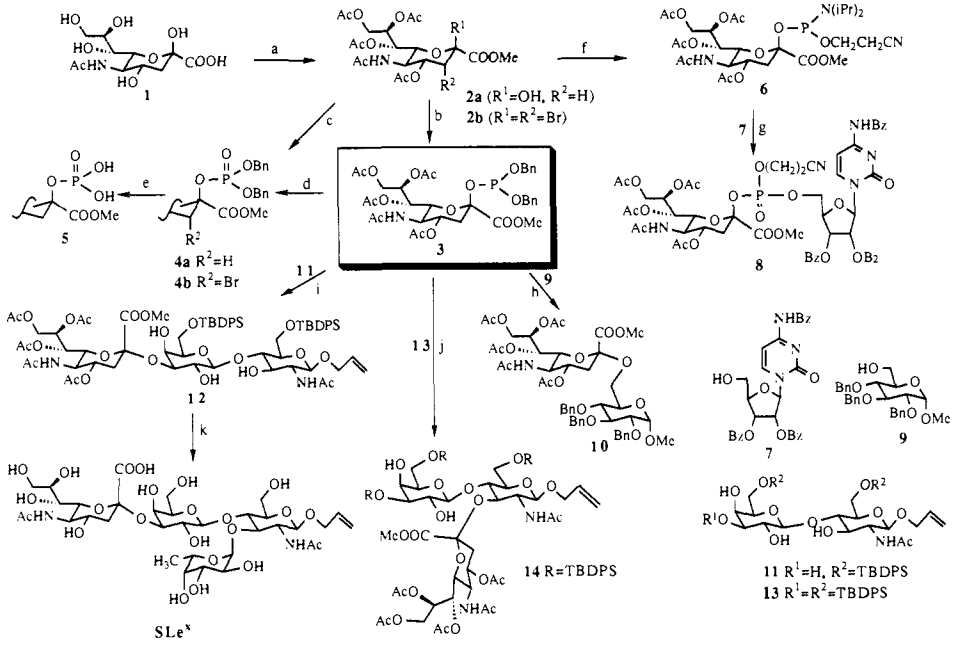
(3) For the synthesis and characterization of DDP, see: Pederson, R. L.; Esker, J.; Wong, C.-H. *Tetrahedron* **1991**, *47*, 2643. This reagent was previously described (but not characterized) and used in the synthesis of alkyl phosphates: de Bont, H. B. A.; Veeneman, G. H.; van Boom, J. H.; Liskamp, R. M. J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 641. Perich, J. W.; Johns, R. B. *Tetrahedron Lett.* **1987**, *28*, 101. For use in the synthesis of *myo*-inositol phosphates, see: Yu, K.-L.; Fraser-Reid, B. *Tetrahedron Lett.* **1988**, *29*, 979.

(4) (a) For the synthesis of β-fucosyl dibenzyl phosphite, see: Ichikawa, Y.; Sim, M. M.; Wong, C.-H. *J. Org. Chem.* **1992**, *57*, 2943. Some diglycosyl phosphites were reported: Ogawa, T.; Akinori, S. *Carbohydr. Res.* **1982**, *110*, C1. Westerduin, P.; Veeneman, G. H.; Marugg, J. E.; Van der Marel, G. A.; van Boom, J. H. *Tetrahedron Lett.* **1986**, *27*, 1211. A protected α-glucosyl dimethyl phosphite was described without isolation and suggested to be an unstable intermediate: Paulsen, H.; Thiem, J. *Chem. Ber.* **1973**, *106*, 115.

(5) (a) Herrler, G.; Gross, H.-J.; Imhof, A.; Brossmer, R.; Milks, G.; Paulson, J. C. *J. Biol. Chem.* **1992**, *267*, 12501. (b) Gross, J.; Brossmer, R. *Eur. J. Biochem.* **1988**, *177*, 583.

0002-7863/92/1514-8748$03.00/0

Scheme I[a]



[a] Reagents and conditions: (a) Dowex 50W × 8 (H^+), MeOH, then $HClO_4$, Ac_2O (78%); for **2b** see ref 8; (b) from **2a**, dibenzyl *N,N*-diethylphosphoramidite (2.3 equiv), 1*H*-tetrazole (4 equiv), THF, room temperature (70%); (c) from **2b**, dibenzyl phosphate (1.2 equiv), 1,1,3,3-tetramethylurea (2.2 equiv), AgOTf (1.2 equiv), 3-Å molecular sieves, CH_2Cl_2/CH_3CN, room temperature (24%); (d) ^{t}BuOOH/THF, −10 °C to room temperature (95%); (e) 5% Pd/C–EtOH, room temperature (99%); (f) 2-cyanoethyl *N,N*-diisopropylphosphoramidochloridite (1.5 equiv), iPr_2NEt (5 equiv), CH_2Cl_2, 0 °C to room temperature (89%); (g) **7** (0.1 equiv), tetrazole (10 equiv), CH_3CN, then ^{t}BuOOH (10 equiv), −40 °C to room temperature (12%); (h) **9** (1.5 equiv), CH_3CN, 3-Å molecular sieves, TMSOTf (0.2 equiv), −42 °C, 30 min (80%, $\alpha:\beta$ = 5:1) (i) **11** (1.5 equiv), same conditions as h (78%, $\alpha:\beta$ = 6:1); (j) **13** (1.5 equiv), same as h (80%, $\alpha:\beta$ = 6:1); (k) (1) Bu_4NF, (2) 1 N NaOH, (3) GDP-Fuc (1.2 equiv), $MnCl_2$ (20 mM), ATP (5 mM), pH 7.5, α1,3-fucosyltransferase (85%).

As shown in Scheme I, treatment of acetylated NeuAc **2a**[6] with DDP and tetrazole in THF gave β-sialyl dibenzyl phosphite **3**[7] (70% yield), which was subsequently converted to phosphates **4a** and **5** via oxidation and hydrogenolysis. Alternatively, **5** was prepared from **2b**[8] via reaction with dibenzyl phosphate to give **4b**, which was then converted to **5** via a radical-mediated reduction. Phosphoramidite **6** synthesized from **2a** via reaction with 2-cyanoethyl *N,N*-diisopropylphosphoramidochloridite[9] was reacted with **7** followed by oxidation to give CMP–sialic acid **8**.

For sialylation, compound **3** was reacted with **9** in the presence of 0.2 equiv of TMSOTf in CH_3CN at −42 °C for 30–40 min to give a 5:1 ($\alpha:\beta$) mixture of the 2,6-linked sialoside **10** in 80% yield based on **3** (85% based on consumed **9**) and the elimination product 2,3-dehydrosialic acid in 5%. No sialylation was observed under such conditions using phosphate **4a** as a glycosylation reagent, though glycosylation (~35%, $\alpha:\beta$ = 3:1) and elimination (~12%) occurred in the presence of stoichiometric amounts of TMSOTf. Compound **3** was then used in the sialylation of **11**[10] under the same conditions to give a 6:1 ($\alpha:\beta$) mixture of the 2,3-linked product **12** in 78% yield based on consumed **11** (33% based on **3**). Interestingly, sialylation of **13** occurred regioselectively at the 3-OH group of GlcNAc to give a 6:1 ($\alpha:\beta$) mixture of the α2,3-linked sialoside **14** in 80% yield (44% based on **3**). Deprotection of **12** followed by enzymatic fucosylation using α1,3-fucosyltransferase gave SLe^x in 85% yield.[11,12]

In summary, we have developed a new chemoenzymatic strategy for the synthesis of CMP–sialic acid and sialosides based on sialyl phosphoramidite and sialyl phosphite/glycosyltransferases. The phosphite is easy to prepare and stable to handle, and the yields of sialylation with **3** are higher than or comparable to those with other sialylation reagents.[2] To further improve the stereoselectivity in the sialylation reaction, one may use the benzyl ester of the NeuAc derivative[11c] or lower the temperature and change the solvent. Other acetylated glycosyl phosphites have been prepared from their peracetates via selective deprotection at C-1 with benzylamine[13] or lipases,[1p,4a] and their application to glycosylation will be published in due course. The strategy described here combined with the readily available sialic acid analogs prepared from the sialic acid aldolase reactions[1p-r] should enable us to

(6) Prepared from sialic acid using Dowex 50 × 8 (H^+)/MeOH–$HClO_4/Ac_2O$, 78% yield. Kuhn, R.; Lutz, P.; MacDonald, D. L. *Chem. Ber.* **1966**, *99*, 611. Marra, A.; Sinay, P. *Carbohydr. Res.* **1989**, *190*, 317.

(7) Data for **3**: ^{1}H NMR ($CDCl_3$) δ 1.79, 1.96, 2.01, 2.06, 2.07 (3 H each, s, OAc and NAc), 2.39 (1 H, dd, J = 4.9, 13.0 Hz, H-3eq), 3.73 (3 H, s, COOMe), 3.74 (1 H, dd, J = 2.0, 10.6 Hz, H-6), 3.99 (1 H, ddd, J = 10.04, 10.4, 10.6 Hz, H-5), 4.10 (1 H, dd, J = 7.4, 12.4 Hz, H-9), 4.32 (1 H, d, J = 10.4 Hz, NH), 4.57 (1 H, dd, J = 2.0, 12.4 Hz, H-9′), 4.83–4.91 (2 H, m, H-4, H-8), 4.93–4.98 (2 H, m, benzylic protons), 5.14 (1 H, dd, J = 2.0, 2.4 Hz, H-7), 5.19 (2 H, dd, J = 9.7, 9.8 Hz, benzylic protons), 7.25–7.50 (10 H, m, phenyl protons); HRMS calcd for $C_{34}H_{42}NO_{15}$ PCs (M + Cs^+) 868.1346, found 868.1346.

(8) Okamoto, K.; Kondo, T.; Goto, T. *Tetrahedron* **1987**, *43*, 5909.

(9) Sinha, N. D.; Biernat, J.; McManus, J.; Koster, H. *Nucleic Acids Res.* **1984**, *12*, 4539. For other phosphoramidite reagents: Letsinger, R. L.; Lunsford, B. *J. Am. Chem. Soc.* **1976**, *98*, 3655. Hecker, S. J.; Minich, M. L.; Lackey, K. *J. Org. Chem.* **1990**, *55*, 4904. Lyttle, M. H.; Wright, P. B.; Sinha, N. D.; Bain, J. D.; Chamberlin, A. R. *J. Org. Chem.* **1991**, *56*, 4608.

(10) Prepared (46% isolated yield) from the β-galactosyltransferase reaction product *N*-acetyllactosamine-β-*O*-allyl (Wong, C.-H.; Ichikawa, Y.; Krach, T.; Gautheron, C.; Dumas, D. P.; Look, G. C. *J. Am. Chem. Soc.* **1991**, *113*, 8137) by reaction with 2 equiv of ^{t}Bu(Ph)$_2$SiCl and imidazole in DMF at room temperature.

(11) SLe^x is a ligand for the adhesion molecule ELAM-1: Phillips, M. L.; Nudelman, E.; Gaeta, F. C. A.; Perez, M.; Singhal, A. K.; Hakomori, S.; Paulson, J. C. *Science* **1990**, *250*, 1130. It is potentially useful as an antiinflammatory agent. For recent synthesis, see: (a) Kameyama, A.; Ishida, H.; Kiso, M.; Hasegawa, A. *J. Carbohydr. Chem.* **1991**, *10*, 549. (b) Nicolaou, K. C.; Hummel, C. W.; Bockovich, N. J.; Wong, C.-H. *J. Chem. Soc., Chem. Commun.* **1991**, *10*, 870. (c) Danishefsky, S. J.; Gervay, J.; Peterson, J. M.; McDonald, F. E.; Koseki, K.; Oriyama, T.; Griffith, D. A.; Wong, C.-H.; Dumas, D. P. *J. Am. Chem. Soc.*, in press. These papers all indicate the same regioselectivity of sialylation with different sialylation reagents. (d) Dumas, D. P.; Ichikawa, Y.; Wong, C.-H.; Weston, B. W.; Lowe, J. B. *Bioorg. Med. Chem.* **1991**, *1*, 425. (e) Wong, C.-H.; Dumas, D. P.; Ichikawa, Y.; Koseki, K.; Danishefsky, S. J.; Weston, B. W.; Lowe, J. B. *J. Am. Chem. Soc.* **1992**, *114*, 7321. (f) Ball, G. E.; O'Neill, R. A.; Schultz, J. E.; Lowe, J. B.; Weston, B. W.; Nagy, J. O.; Brown, E. G.; Hobbs, C. J.; Bednarski, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5449.

(12) The ^{1}H NMR data of SL^x are identical to those of the compound prepared previously; see ref 11e.

(13) Helferich, B.; Portz, W. *Chem. Ber.* **1953**, *86*, 604.

incorporate unnatural sialic acids into oligosaccharides.

Acknowledgment. This work was supported by the NIH (GM44154) and Cytel Co., San Diego, CA.

Supplementary Material Available: A listing of complete experimental details and analytical and spectral data for all new compounds (**3–8, 11–14**) (9 pages). Ordering information is given on any current masthead page.

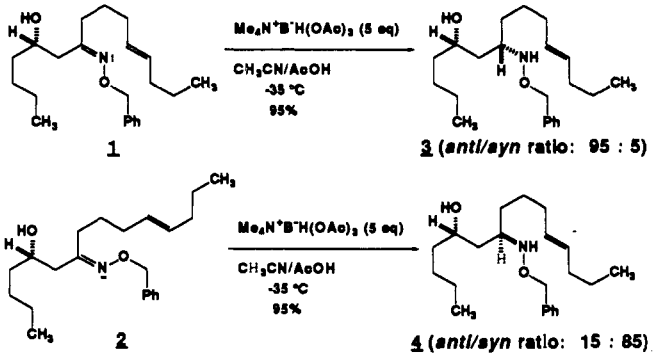
Stereocontrolled Hydride Reductions of β-Hydroxy Oximino Ethers

David R. Williams* and Martin H. Osterhout

Department of Chemistry, Indiana Univeristy
Bloomington, Indiana 47405

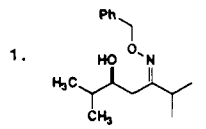
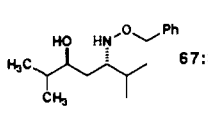
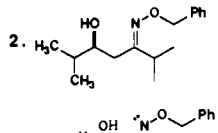
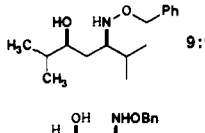
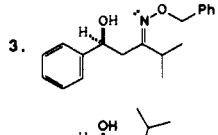
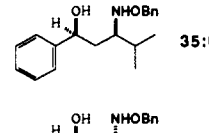
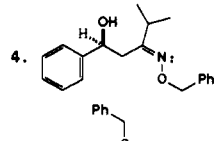
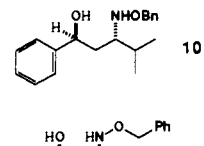
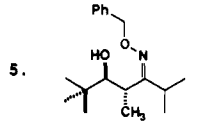
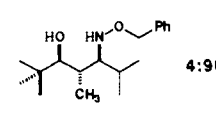
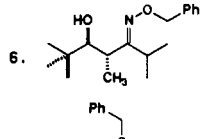
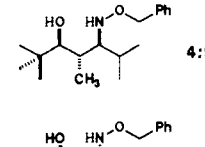
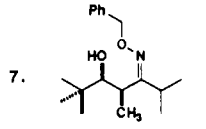
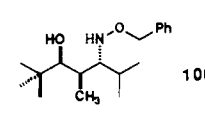
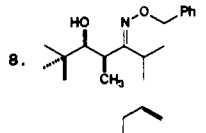
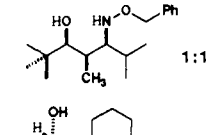
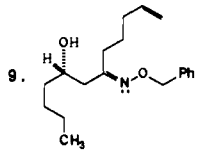
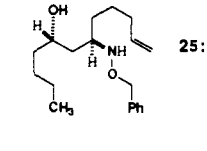
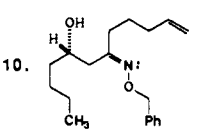
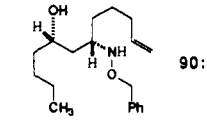
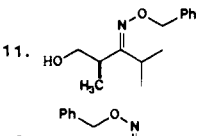
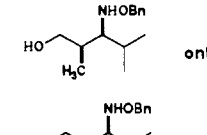
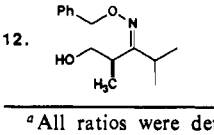
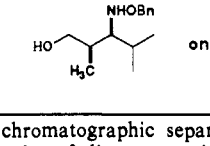
Received June 15, 1992

In recent years, the development of "internally-directed" reagents through participation of a proximate hydroxyl function has afforded fundamental advances for directed epoxidations, hydrogenations, hydride reductions, and conjugate additions. Naraska[1] and Evans[2] have reported complementary reagent-based strategies for preparation of 1,3-*syn*- and 1,3-*anti*-diols via reductions of acyclic β-hydroxy ketones. Additional developments have been reported which continue to expand the scope of stereoselective reductions to provide 1,3-diols and related derivatives.[3] In connection with our interest in alkaloid synthesis, we have examined opportunities for preparation of 1,3-amino alcohols wherein the diastereofacial selectivity of hydride delivery to an imino (C=N) bond is affected by a neighboring hydroxyl group.[4] Herein, we illustrate our findings for 1,3-asymmetric induction in reductions of β-hydroxy oximino ethers. Our initial observations resulted from individual reductions of pure (*Z*)- and (*E*)-oximino benzyl ethers **1** and **2** with tetramethylammonium triacetoxyborohydride (TABH) in anhydrous acetic acid–acetonitrile (1:1



by volume) at −35 °C. (*Z*)-Oxime **1** afforded smooth conversion to the 1,3-anti product **3**, while the corresponding (*E*)-oxime **2** gave mostly the 1,3-syn arrangement **4**.[5] Diastereoselectivity was achieved based upon geometry of the starting oximino ethers.

Table I. Diastereofacial Hydride Reduction of β-Hydroxy Oximino Ethers

Entry	Oxime	Rxn. Conditions	Major Product[a]	Ratio[b] (anti:syn)	Yield
1.		TABH (5 eq) -35 °C; 6 hr then 22 °C; 1 hr		67:33	100%
2.		TABH (5 eq) -35 °C; 6 hr then 22 °C; 1 hr		9:91	94%
3.		TABH (5 eq) -35 °C; 6 hr		35:65	95%
4.		TABH (5 eq) -35 °C; 6 hr		100:1	92%
5.		TABH (8 eq) -15 °C; 12 hr then 22 °C; 2 hr		4:96	94%
6.		TABH (8 eq) -15 °C; 12 hr then 22 °C; 2 hr		4:96	93%
7.		TABH (10 eq) -35 °C; 4 hr then 22 °C; 4 hr		100:1	75%
8.		TABH (8 eq) -35 °C; 4 hr then 22 °C; 4 hr		1:100	27%[c]
9.		TABH (5 eq) -35 °C; 6 hr		25:75	85%
10.		TABH (5 eq) -35 °C; 6 hr		90:10	90%
11.		TABH (5 eq) -35 °C; 4 hr		only	92%
12.		TABH (5 eq) -35 °C; 4 hr		only	93%

[a] All ratios were determined by chromatographic separation and product isolations. In some cases ratios of diastereomeric products were also confirmed by ^{1}H NMR of crude mixtures. [b] Anti/syn products were identified by ^{1}H NMR and conversion to their cyclic carbamates (carbonyldiimidazole, benzene, heat) for proton decoupling studies. [c] Largely starting oxime (70%) was recovered.

This behavior is typical for a variety of substrates as summarized in Table I. Yields generally range from 80–95%. In cases of lower yields, considerable amounts of starting oxime ethers were recovered. Such examples (entry 8) exhibited significant steric interactions and very slow reaction times. In all cases of incomplete reactions, reisolated oximes showed no evidence of *E*/*Z* isomerization under the reaction conditions. The significance of

(1) Narasaka, K.; Pai, F.-C. *Tetrahedron* **1984**, *40*, 2233.
(2) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560 and references therein. Evans, D. A.; Hoveyda, A. H. *J. Org. Chem.* **1990**, *55*, 5190.
(3) Mohr, P. *Tetrahedron Lett.* **1991**, *32*, 2219. Boger, D. L.; Curran, T. T. *J. Org. Chem.* **1992**, *57*, 2235. Evans, D. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1990**, *112*, 6447.
(4) Narasaka, K.; Ukaji, Y.; Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 525.
(5) The individual *anti*- and *syn*-oxime isomers were separated by silica gel flash chromatography. Determination of oxime geometry was based on ^{13}C and ^{1}H NMR data. The assignments of chemical shifts of α-carbons located syn to the benzyloxy substituent are observed upfield relative to the corresponding anti isomers due to steric compression. Proton signals for α-methylene units of *syn*-oximino benzyl ethers appear at slightly lower field compared to the anti isomers. Karabatsos, G. J.; Hsi, N. *Tetrahedron* **1967**, *23*, 1079. See, also: ref 4.

0002-7863/92/1514-8750$03.00/0