vertically provided uniform wetting of the substrate in the well area and favored heterogeneous film growth. The films prepared by parallel synthesis were shown to have similar morphology to those synthesized under conventional conditions but their X-ray diffraction patterns indicate lesser orientation of crystallites. Parallel synthesis was used to screen the composition space of organic-free clear synthesis solution for ZSM-5 film growth. The composition SiO_2:(0.5–0.7) NaOH:(1/300–1/700) Al_2O_3:80 H_2O resulted in continuous ZSM-5 films of Si/Al ~ 20:1.

Experimental Section

Two types of silicon sources were used: sodium silicate solution (14% NaOH and 27% SiO_2), and tetraethylorthosilicate (TEOS). Sodium silicate was filtered by using a Buchner funnel with a coarse fritted disc immediately before use. When TEOS was used as the silicon source, it was first dissolved in tetrapropylammonium hydroxide (TPAOH) to form a clear solution of composition TEOS:0.15 TPAOH:0.7 NaOH:98 H_2O, which was then filtered before use with a PTFE filter (0.45 μm). Tetrapropylammonium bromide (TPABr) solution (25 wt%) was prepared and filtered with 0.45 μm cellulose acetate membranes.

The synthesis mixture was prepared by mixing a measured amount of chemicals in a transparent LDPE vial of volume 1 mL (Nalgene). When sodium silicate solution was used, H_2SO_4 (5 N, VWR) was added to adjust the alkalinity of the final solution. After thorough shaking, a clear synthesis solution was formed and aged for one day at room temperature without stirring before being introduced into the well for reaction. Occasionally, the synthesis mixtures turned turbid immediately after mixing, but the solution became clear after standing for several hours.

The substrates employed were nonporous α-alumina disks of diameter 2.5 cm. Prior to seeding the substrates were cleaned by a procedure described in reference [22]. Seeding of the entire substrate surface with a monolayer of silicalite particles was carried out using a previously developed protocol.[12, 33] The seeds about 0.4 μm in size were finer than the substrate roughness and did not cause problems in sealing under pressure against the Teflon surfaces.

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Bowl-Shaped Tris(2,6-diphenylbenzyl)tin Hydride: A Unique Reducing Agent for Radical and Ionic Chemistry**

Kouji Sasaki, Yuichiro Kondo, and Keiji Maruoka*

Trialkyltin hydrides (R_3SnH) are widely utilized in numerous radical reactions including reductive dehalogenations,[1, 2] desulfurizations,[3] and radical cyclizations.[4] Among several R_3SnH (R = Me, Bu, Ph), Bu_3SnH is the most popular reagent in radical chemistry. The Bu_3SnH-mediated radical reactions exhibit high regio- and stereoselectivity by changing radical initiators (azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), *hν*, Et_3B, etc.) and/or the reaction conditions.[5] Alternatively, such stereoselectivity is also achievable by replacing Bu_3SnH or Ph_3SnH[6] with the sterically more hindered $(Me_3Si)_3SiH$.[7] However, it is apparent that there

[*] Prof. K. Maruoka, K. Sasaki, Y. Kondo
Department of Chemistry, Graduate School of Science
Kyoto University
Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-4041
and
Department of Chemistry, Graduate School of Science
Hokkaido University
Sapporo, 060-0810 (Japan)
E-mail: maruoka@kuchem.kyoto-u.ac.jp

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is a limit to such steric approaches due to the troublesome introduction of sterically hindered alkyl groups in the preparation of bulky R_3SnH. In this context, we have focused on the possibility of using a bowl-shaped trialkyltin hydride of type **2** to obtain high stereoselectivity by remote steric control as illustrated by the stereoselective reduction of vinyl radical **1** (Scheme 1). Herein we report that the bowl-shaped tris(2,6-diphenylbenzyl)tin hydride (TDTH) can be successfully utilized as a new reducing agent, and in particular achieves a unique selectivity not observable in ordinary radical and ionic reactions involving previously known R_3SnH and $(Me_3Si)_3SiH$.[8–11]

The requisite TDTH can be conveniently prepared from commercially available 2-chloro-6-phenyltoluene in the four-step sequence shown in Scheme 2. The structure of TDTH, which was determined by single-crystal X-ray diffraction analysis (Figure 1),[12] reveals the presence of a molecular pocket about the tin atom.

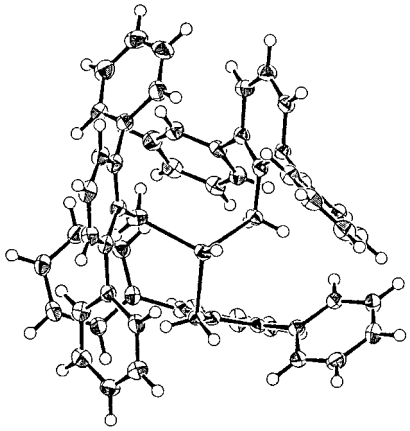
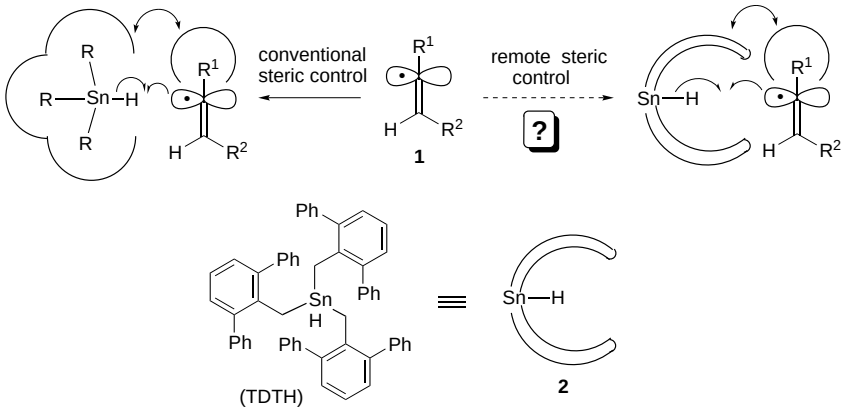
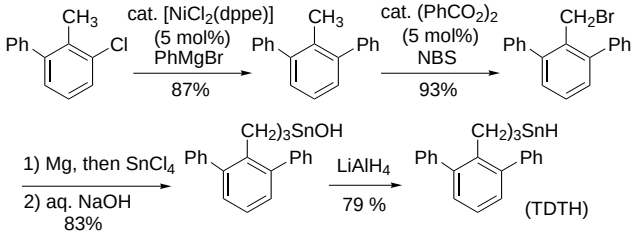


Figure 1. Structure of TDTH (ORTEP representation).



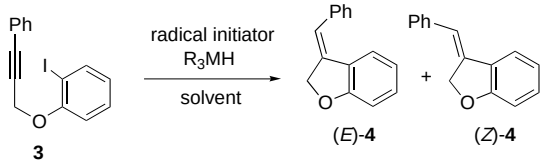
Scheme 1. Bowl-shaped tris(2,6-diphenylbenzyl)tin hydride (TDTH) (**2**) allows the remote stereochemical control in vinyl radical reductions.



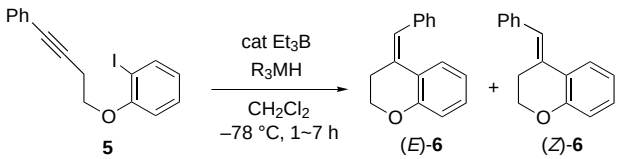
Scheme 2. Four-step synthesis of TDTH from commercially available 2-chloro-6-phenyltoluene. dppe = 1,2-bis(diphenylphosphanyl)ethane; NBS = *N*-bromosuccinimide.

Intramolecular radical cyclization of the *o*-halophenyl ether, *o*-iodophenyl 3-phenylpropynyl ether (**3**) under standard radical reaction conditions (catalytic AIBN (0.2 equiv), Bu_3SnH (1.1 equiv), benzene reflux) gave rise to an *E*/*Z* mixture of cyclic ether **4** in 99% yield (*E*/*Z* = 1:37; Scheme 3).[13] Reaction of **3** in CH_2Cl_2 with Bu_3SnH or Ph_3SnH (1.1 equiv) and catalytic Et_3B (0.4 equiv) as radical initiator at $-78\,^{\circ}C$ yielded **4** in 88 ~ 99% yield with moderate stereoselectivity (*E*/*Z* = 3.1 ~ 5.1:1). Switching R_3SnH (R = Bu, Ph) to bulky $(Me_3Si)_3SiH$ (1.1 equiv) further enhanced the selectivity to *E*/*Z* = 10.8:1 at the expense of chemical yield (38%). In marked contrast, however, radical reduction of **3** with TDTH (1.1 equiv) and catalytic Et_3B (0.5 equiv) in CH_2Cl_2 afforded **4** in 97% yield with excellent stereoselectivity (*E*/*Z* = 46.5:1), implying the importance of our new strategy on remote stereochemical control to achieve high selectivity of the radical cyclization.[14]

We also examined the intramolecular cyclization of the one-carbon elongated *o*-halophenyl ether, *o*-iodophenyl 4-phenylbutynyl ether (**5**), which can be categorized as a heptynyl radical cyclization (Scheme 4). Interestingly, radical cyclization of **5** with Bu_3SnH gave the target cyclic ether **6** with low selectivity (*E*/*Z* = 1.5:1),



Scheme 3. Influence of R_3MH on the radical cyclization of **3** to **4**. Reagents, conditions, and selectivities: cat. AIBN/Bu_3SnH/benzene, 80 °C, 1 h: 99% (*E*/*Z* = 1:37); cat. Et_3B/Bu_3SnH/CH_2Cl_2, −78 °C, 2 h: 99% (*E*/*Z* = 5.1:1); cat. Et_3B/Ph_3SnH/CH_2Cl_2, −78 °C, 2 h: 88% (*E*/*Z* = 3.1:1); cat. Et_3B/$(Me_3Si)_3SiH$/CH_2Cl_2, −78 °C, 3 h: 38% (*E*/*Z* = 10.8:1); cat. AIBN/TDTH/benzene, 80 °C, 2.5 h: 57% (*E*/*Z* = 22.8:1); cat. Et_3B/TDTH/CH_2Cl_2, −78 °C, 2.5 h: 97% (*E*/*Z* = 46.5:1).



Scheme 4. Influence of R_3MH on the radical cyclization of **5** to **6**. Reagents, conditions, and selectivities: cat. Et_3B (0.2 equiv)/Bu_3SnH (1.1 equiv): 71% (*E*/*Z* = 1.5:1); cat. Et_3B (1 equiv)/$(Me_3Si)_3SiH$ (1.1 equiv): 57% (*E*/*Z* = 44:1); cat. Et_3B (0.6 equiv)/TDTH (1.1 equiv): 76% (*E*/*Z* = > 100:1).

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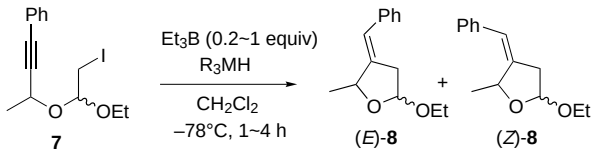
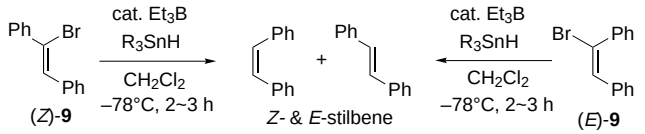
whereas use of TDTH afforded **6** with virtually complete stereoselectivity ($E/Z = > 100{:}1$).

A similar tendency is also observed in the stereoselective radical cyclization of iodoacetal **7** (diastereomeric ratio = 1:1) to cyclic acetal **8** (diastereomeric ratio = 1:1) with high Z selectivity using TDTH (Scheme 5).



Scheme 5. Influence of R_3MH on the radical cyclization of **7** to **8**. Reagents, conditions, and selectivities: cat. Et_3B (0.2 equiv)/Bu_3SnH (1.2 equiv): 92% ($E/Z = 1{:}3.1$); cat. Et_3B (0.2 equiv)/Ph_3SnH (1.2 equiv): 98% ($E/Z = 1{:}4.3$); cat. Et_3B (1 equiv)/$(Me_3Si)_3SiH$ (1.2 equiv): 76% ($E/Z = 1{:}6.7$); cat. Et_3B (1 equiv)/TDTH (1.2 equiv): 76% ($E/Z = 1{:}65.8$).

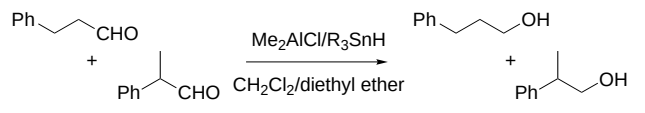
Such selectivity in vinyl radical reduction appears feasible in acyclic systems. For example, E-bromostilbene is transformed to Z-stilbene with excellent stereoselectivity ($Z/E = > 100{:}1$) on treatment with TDTH (1.1 equiv) and catalytic Et_3B (0.2 equiv) in CH_2Cl_2 at low temperature, while the selectivity is only moderate ($Z/E = 3.4{:}1$) in the case of Bu_3SnH under similar reduction conditions (Scheme 6).



93% (Z/E = 3.4 : 1)	cat Et_3B/Bu_3SnH	95% (Z/E = 3.4 : 1)
82% (Z/E = 92.4 : 1)	cat Et_3B/TDTH	74% (Z/E = >100 : 1)

Scheme 6. Influence of R_3MH on the selectivity in the vinyl radical reduction of acyclic systems.

The synthetic power of TDTH has been further demonstrated in ionic reactions by the chemoselective, electrophilic reduction of structurally similar aldehyde substrates with trialkyltin hydride. For example, treatment of one equivalent each of hydrocinnamaldehyde and α-phenylpropionaldehyde in CH_2Cl_2/diethyl ether (v/v, 7/1) with R_3SnH (R = Bu, Ph; 1 equiv) under the influence of Me_2AlCl (2.2 equiv) as Lewis acid at low temperature afforded a mixture of less hindered 3-phenyl-1-propanol and more hindered 2-phenyl-1-propanol with only moderate selectivity (Scheme 7).[15] However,



Scheme 7. Influence of R_3MH on the chemoselective, electrophilic reduction of similar aldehyde substrates. Reagents, conditions, and selectivities: Bu_3SnH, –78 °C, 0.5 h: 81% (43:57); Ph_3SnH, –78 °C, 1 h: 93% (38:62); TDTH, –78 ~ –20 °C, 1.5 h: 82% (>100: <1); L-Selectride, –78 °C, 0.5 h: 99% (45:55).

virtually complete discrimination of two structurally different aldehyde carbonyl groups can be realized with TDTH as hydride donor. Notably, an ordinary selective reducing agent, L-Selectride gave a disappointing result in terms of the chemoselectivity.

Experimental Section

Radical cyclization of **3** with TDTH: To the solution of TDTH (280.4 mg, 0.33 mmol) in CH_2Cl_2 (2.5 mL) was added **3** (100.2 mg, 0.3 mmol) in CH_2Cl_2 (1 mL) and Et_3B (150 μL, 0.15 mmol of a 1M solution in hexane) under Ar at –78 °C. After the reaction mixture had been stirred at –78 °C for 2.5 h, it was poured into an aqueous saturated solution of $NaHCO_3$ and then extracted with diethyl ether. The combined extracts were dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography on silica gel (diethyl ether/hexane (1/20)) gave **4** as a colorless oil and a small amount of **3** which was recovered (**4**: 60.8 mg, 0.292 mmol, 97% yield; **3**: 0.008 mmol, 3% yield). The ratio of (*E*)/(*Z*)-**4** was determined by ^{1}HNMR analysis ((*E*)/(*Z*)-**4** = 46.5/1.0). (*E*)-**4**; ^{1}HNMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.45 - 7.20$ (m, 6H; Ar-H), 7.16 (t, $J(H,H) = 7.8$ Hz, 1H; Ar-H), 6.86 (d, $J(H,H) = 7.8$ Hz, 1H; Ar-H), 6.68 (t, $J(H,H) = 7.8$ Hz, 1H; Ar-H), 6.50 (t, $J(H,H) = 2.5$ Hz, 1H; C=CHPh), 5.24 (d, $J(H,H) = 2.5$ Hz, 2H; C=CH_2O); (*Z*)-**4**; $\delta = 7.53$ (d, $J(H,H) = 7.6$ Hz, 1H; Ar-H), 7.41 (t, $J(H,H) = 7.8$ Hz, 2H; Ar-H), 7.32 – 7.20 (m, 4H; Ar-H), 6.96 (t, $J(H,H) = 7.6$ Hz, 1H; Ar-H), 6.92 (d, $J(H,H) = 7.6$ Hz, 1H; Ar-H), 6.85 (t, $J(H,H) = 3.0$ Hz, 1H; C=CHPh), 5.43 (d, $J(H,H) = 3.0$ Hz, 2H; C=CH_2O).

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[12] The single-crystal of **2** was obtained by recrystallization from diethyl ether. Crystal structure data for **2**: $C_{57}H_{46}Sn$, $M_r = 849.68$, triclinic, space group $P\bar{1}$, $a = 12.894$, $b = 14.512$, $c = 12.858$ Å, $V = 2097.810$ Å^3, $Z = 2$, $\rho_{calcd} = 1.35\ g\,cm^{-1}$, $R_1 = 0.05$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152190. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] Treatment of (*E*)-**4** (*E*/*Z* = 46.5:1) with Bu_3SnH (1 equiv) in benzene under reflux for 2 h gave rise to an *E*/*Z* mixture (*E*/*Z* = 2:1) of **4**, suggesting that (*Z*)-**4** is a thermodynamic product.

[14] TDTH was found to be a slower reducing agent than Bu_3SnH. For example, reduction of benzyl *p*-iodophenyl ether with Bu_3SnH and TDTH (1.1 equiv) in CH_2Cl_2 at −78 °C under the influence of catalytic Et_3B (0.2 equiv) for 20 min afforded benzyl phenyl ether in 88% and 40% (recovery of *p*-iodophenyl ether in 56%) yields, respectively.

[15] Attempted reduction of the two different aldehydes with $(Me_3Si)_3SiH$ in the presence of Me_2AlCl resulted in recovery of most of these aldehydes.

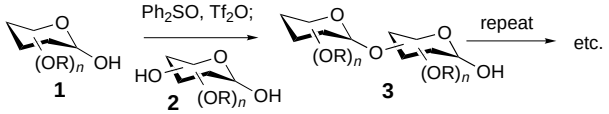
Chemoselective Iterative Dehydrative Glycosylation**

Hien M. Nguyen, Jennifer L. Poole, and David Y. Gin*

The development of strategies for efficient construction of complex oligosaccharides has been a long-standing challenge in organic synthesis.[1] This is a direct result of the immense structural diversity and biological importance of complex glycoconjugates in nature. In traditional approaches to the assembly of oligosaccharides, a preformed glycosyl donor incorporating an anomeric latent leaving group is coupled with a nucleophilic glycosyl acceptor, and the resulting disaccharide then undergoes either a selective deprotection or anomeric derivatization step prior to the subsequent coupling event. In order to streamline this process, a number of elegant chemoselective and orthogonal glycosylation strategies have been developed with the goal of circumventing deprotection and anomeric derivatization steps in the iterative glycosylation sequence. Within this context, two key strategies, which use well-established glycosylation methods, have been explored. One approach employs carbohydrate coupling partners with identical anomeric latent leaving groups; the reactivities of each of the leaving groups are differentiated by varying the electronic nature of proximal protective groups.[2] The success of this approach to oligosaccharide synthesis thus relies on intricate selection of protective groups to establish a suitable reactivity hierarchy among the carbohydrate building blocks.[2e] In an alternative strategy, the anomeric latent leaving groups in the carbohydrate coupling partners are mutually distinct, possessing chemically orthogonal reactivities; successive glycosylations are performed with a number of different reagents that are specific for a certain latent leaving group.[3]

We now report a novel approach to iterative oligosaccharide synthesis which employs a chemoselective glycosylation strategy that: 1) is not dependent on the careful selection and placement of specific protective groups in the carbohydrate coupling partners to electronically influence anomeric reactivity; 2) avoids the need for C1-derivatized carbohydrate building blocks with chemically distinct anomeric latent leaving groups; and 3) requires only a single glycosylation method to effect iterative one-pot anomeric bond constructions.

We have recently established a dehydrative glycosidic coupling method whereby a variety of nucleophilic acceptors can be directly glycosylated with C1-hydroxy donors using diphenyl sulfoxide and triflic anhydride.[4, 5] The fact that our dehydrative coupling is not plagued by self-condensation of the C1-hydroxy donor led us to investigate the possibility of selective glycosylation of an alkyl hydroxy group in the presence of a free hemiacetal functionality. In this context, our dehydrative glycosylation reaction can serve as the basis for a new approach to iterative chemoselective glycosylation in which a hemiacetal donor **1** is activated with diphenyl sulfoxide and triflic anhydride (Scheme 1). A nucleophilic



Scheme 1. Chemoselective iterative dehydrative glycosylation. Tf = trifluoromethanesulfonyl.

acceptor **2**, which incorporates a free alkyl hydroxy group as well as an unprotected C1-hemiacetal functionality, is then introduced. Ideally, the alkyl alcohol is chemoselectively glycosylated in the presence of the hemiacetal hydroxy group to generate, in a one-pot procedure, the hemiacetal-terminated disaccharide **3**, which is immediately poised for another coupling iteration. Thus, the key issue of chemoselectivity in this approach pertains only to the relative nucleophilicities of the alkyl hydroxy group versus the hemiacetal hydroxy group

[*] Prof. D. Y. Gin, H. M. Nguyen, J. L. Poole
Department of Chemistry
University of Illinois
Urbana, IL 61801 (USA)
Fax: (+1) 217-244-8024
E-mail: gin@scs.uiuc.edu

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