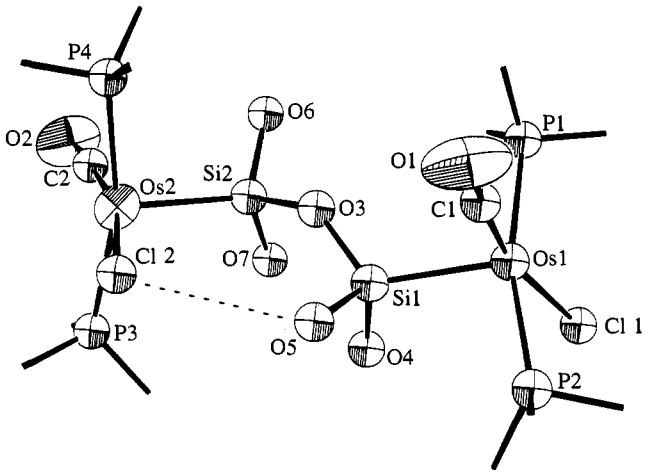

Figure 2. ORTEP view of **4** with the phenyl rings of the PPh_3 ligands omitted for clarity. Thermal ellipsoids at the 50% probability level. Important distances (Å) and angles (deg): Os(1)-Si(1), 2.318 (5); Si(1)-O(3), 1.637 (10); Os(2)-Si(2), 2.337 (5); Si(2)-O(3), 1.645 (10); Si(1)-O(3)-Si(2), 137.9 (7).

this may be attributed to both the electronegative substituents on silicon and the fact that the complex is only five coordinate.[4a,b,10] Within the trihydroxysilyl group, all three Si-O distances and Os-Si-O angles are very close to normally observed values.[5,10,11] Importantly, there is no indication of any interaction between the oxygen atoms and the coordinatively unsaturated osmium center.

A remarkable feature of the structure of **2** is that the trihydroxysilyl group is not involved in any significant hydrogen-bonding interactions to oxygen or chlorine. The intramolecular O(2)-Cl distance of 3.65 Å falls well outside the range of 2.92-3.18 Å observed for typical O-H···Cl hydrogen bonds.[12] The closest intermolecular approaches involving the $Si(OH)_3$ oxygen atoms are those made to the carbon atoms of an adjacent triphenylphosphine ligand (3.32 Å).[13] Only three organosilanetriols have been structurally characterized,[3] and in each case extensive intermolecular hydrogen-bonded networks in the form of sheets or polyhedral cages are evident. The absence of intermolecular hydrogen bonding in **2** is most probably due to the steric shielding afforded by the two mutually trans triphenylphosphine ligands.

If the hydrolysis of **1** is carried out in the presence of less than stoichiometric amounts of aqueous sodium hydroxide, small amounts of the diosmium tetrahydroxydisiloxane $[OsCl(CO)(PPh_3)_2Si(OH)_2]_2O$ (**4**) are formed along with **2**. Much larger yields of this compound (ca. 70%) are obtained if equimolar quantities of **1** and **2** are allowed to react together in water-saturated dichloromethane. Partial or complete hydrolysis of **1** may precede the dimerization step which could be acid catalyzed (Scheme I).

The single-crystal X-ray structure of **4** has been determined,[14] and an ORTEP diagram is shown in Figure 2. Although there are no intermolecular hydrogen bonds evident in the structure, the Cl(2)-O(5) distance of 3.17 Å suggests that this one SiOH group is involved in a weak intramolecular hydrogen bond to chloride (see Figure 2).[12,15] This interaction may be responsible for the relatively small Si-O-Si angle in **4** as well as the difference (which is probably significant) in the two Os-Si distances.

The two new compounds **2** and **4** can be viewed as derivatives of orthosilicic acid (H_4SiO_4) and pyrosilicic acid ($H_6Si_2O_7$), respectively, in which one of the hydroxy groups on each silicon atom has been substituted by a transition metal, viz. $L_nMSi(OH)_3$ and $L_nMSi(OH)_2OSi(OH)_2ML_n$. As such they represent the first examples of these new classes of compounds. The unused functionality at silicon in these compounds and the coordinative unsaturation at osmium offer many opportunities for further synthetic transformations, and these possibilities are being explored.

Acknowledgment. We thank the University of Auckland Research Committee for partial support of this work through a grant in aid to W.R.R. and L.J.W.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond angles, and bond distances for **2** and **4**, preparative details, combustion analyses, and IR and ^1H, ^{31}P, and ^{29}Si NMR spectral data for **2** and **4** (14 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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(13) The closest intramolecular approach involving the $Si(OH)_3$ oxygen atoms and the phenyl rings of **2** is 3.17 Å (O(2)-C(26)). π···HO bonding has been considered in other silanol structures: Al-Juaid, S. S.; Al-Nasr, A. K. A.; Eaborn, C.; Hitchcock, P. B. *J. Chem. Soc., Chem. Commun.* **1991**, 1482.

(14) Yellow crystals of **4** were grown by slow diffusion of ethanol into a dichloromethane solution of **4** at 4 °C. Crystal data: a = 10.494 (6), b = 18.316 (3), c = 19.527 (3) Å, α = 92.84 (1), β = 92.86 (2), γ = 101.05 (3)°, Z = 2, d(calcd) = 1.534 g cm^{-3}, space group $P\bar{1}$. A total of 4627 reflections ($I > 3\sigma(I)$) were collected on a Nonius CAD-4 diffractometer at 293 K using Mo Kα radiation (λ = 0.710 69 Å). Least-squares refinement converged to $R(F)$ = 0.049 and $R_w(F)$ = 0.051.

(15) Other intramolecular approaches involving the $Si(OH)_2$ oxygen atoms and the phenyl rings of **4** are O(6)-C(63), 3.04 Å, and O(4)-C(40), 3.20 Å.

Control of Dispersity in Stereoselective Telomerizations: The Addition/Cyclization/Transfer Strategy

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Received August 27, 1992

There are a variety of natural products and organic substructures that possess a carbon skeleton with a precise number of repeating chiral units. Traditional approaches to the construction of these substructures require successive additions of repeating units and can be prohibitively long and inefficient. Free radical telomerization has the potential of connecting multiple repeating units in a single step, but this second approach suffers from two fundamental limitations: (1) difficulty in controlling telomer distribution and (2) lack of stereochemical control. Existing strategies to the telomer distribution problem include the spanning strategy pioneered by Feldman,[1] who has proposed the term *oligoselectivity* to describe size control in oligomerization reactions. A second approach[2,3] employs covalent attachment of monomer units to a template and relies on the potential advantage of intramolecular addition reactions compared to intermolecular reactions.

We have developed a rational strategy that integrates our expertise in both acyclic stereocontrol[4] and radical macro-

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(3) Shea, K. J.; O'Dell, R.; Sasaki, D. Y. *Tetrahedron Lett.* **1992**, *33*, 4699.

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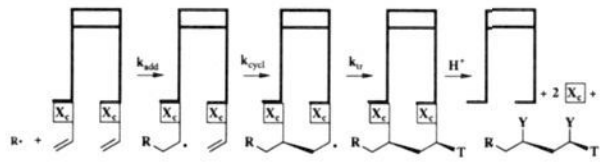
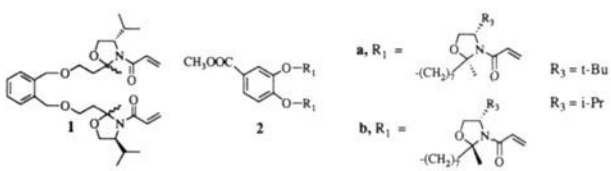


Figure 1. Addition/cyclization/transfer (ACT) strategy.

cyclization[5] (Figure 1). In this strategy, *n* acrylamide monomers are covalently attached through oxazolidine auxiliaries (X_c) to flexible tethers on a rigid base compound. Under normal telomerization conditions, addition of a free radical (R•) to a pendant acrylamide generates a prochiral radical. Subsequent macrocyclization gives a second prochiral radical that is finally trapped with an appropriate chain-transfer reagent (T). Hydrolysis of the reaction products releases the individual components. This approach, which relies on the high effective molarity[6] of intramolecular monomers, has the potential to produce essentially monodisperse telomers with controlled stereochemistry.

Several templates were prepared to provide a survey of structural requirements that are important in the application of the addition/cyclization/transfer strategy. The compounds **2a** (R_3 = *i*-Pr), **2b** (R_3 = *i*-Pr), **2a** (R_3 = *t*-Bu), and **2b** (R_3 = *t*-Bu) were prepared by alkylation of methyl 3,4-dihydroxybenzoate with the requisite bromide.[7] The compound **1** was prepared as a 1.0:3.7:3.0 inseparable mixture of diastereomers at the oxazolidine quaternary carbon.[8]

We initially studied the reaction of **1** with cyclohexyl iodide and allyltri-*n*-butylstannane (**3**), a methodology we applied in demonstrating the efficacy of oxazolidine auxiliaries.[9] The reaction, which could be monitored by GC for both template disappearance and formation of products **4** and **5**, was optimized through systematic variation of template and transfer reagent concentrations. On the basis of these initial results, the reaction



with 2.5 mM **1**, 80 mM $C_6H_{11}I$, and 200 mM **3** was examined in greater detail. The product mixture, which contained **5** resulting from transannular H-atom abstraction[10] following cyclization but preceding chain transfer, was hydrolyzed in refluxing 4 N HCl/*p*-dioxane (1:1) and reacted with diazomethane to give telomers **6**, which were conveniently analyzed by GC/MS.[11] Although products with $n = 2$ made up nearly 70% of the telomers **6**, fully half of the $n = 2$ products had R = H rather than allyl, underscoring the detrimental nature of the benzylic position for this template. The diastereomer ratio for **6** ($n = 2$, R = allyl) formed from **1** was also poor, approximately 2:1.

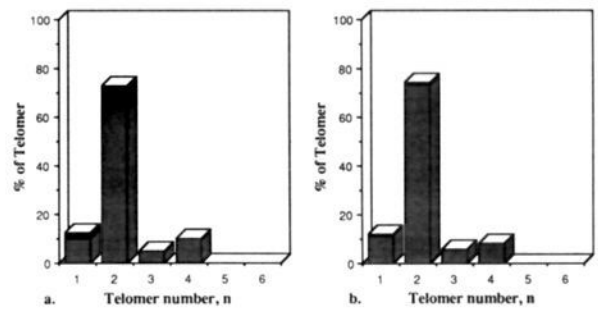
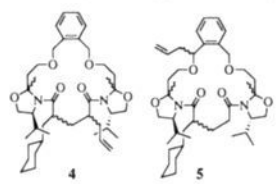
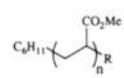


Figure 2. Product histograms for reaction of alkenes with $C_6H_{11}I$ and allylstannane. Gray indicates allyl transfer product, **6** (R = allyl), and black indicates H-transfer product: (a) **2a** (R_3 = *i*-Pr); (b) **2a** (R_3 = *t*-Bu). Standard conditions are 2.5 mM template, 80 mM $C_6H_{11}I$, and 200 mM **3**.





The $n = 2$ product is favored for each template with structure **2**. For **2a** (R_3 = *i*-Pr), products with $n = 2$ make up nearly 80% of the telomer mixture (Figure 2a). Hydrogen atom transfer is still a significant process for this template, with the H:allyl transfer ratio being 1:7. Stereoselectivity was modest for **6** ($n = 2$), as expected for a valinol-derived oxazolidine,[9] the diastereomer ratio being 3:1. The stereoisomer **2b** (R_3 = *i*-Pr) gives significantly less **6** ($n = 2$) product than does **2a**, with allyl transfer competing effectively with cyclization for this template.

The template **2a** (R_3 = *t*-Bu) is the best we have examined to date. Thus, **6** ($n = 2$, R = allyl) is formed with good chemoselectivity, oligoselectivity (teloselectivity), and stereoselectivity for this substrate. The two diastereomers of **6** ($n = 2$, R = allyl) are formed in a ratio of 22:1, the one major product of the sequence making up over 75% of the telomer mixture (Figure 2b).[12] Products from the stereoisomer **2b** (R_3 = *t*-Bu) give somewhat more **6** ($n = 1$, R = allyl; data not shown). Significantly, H-atom transfer is essentially eliminated for reactions using *t*-Bu oxazolidines. While the improved stereoselectivity of oxazolidines having R_3 = *t*-Bu was expected, reduction of H-atom transfer observed for this auxiliary was unanticipated.

The addition/cyclization/transfer strategy illustrated here provides a reasonably quick entry to substructures having two isotactic 1,3-stereogenic centers. Preliminary studies with methyl gallate derived templates having three acrylamide pendant groups indicate a preponderance of **6** ($n = 3$, R = allyl) products in these reactions. Efforts are also underway to construct assemblies that lead stereoselectively to higher telomers having template-defined nonisotactic geometries.

Acknowledgment. Support of this research by NIH and NSF is gratefully acknowledged. G.S.M. acknowledges receipt of a fellowship from Tennessee Eastman. We thank Drs. K. Drauz

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(7) Details of the synthesis of representative templates are presented in the supplementary material. The assignment of stereochemistry to the oxazolidines **a** or **b** is not definitive and is based on nuclear Overhauser effect enhancement of the cross ring methyl when the *tert*-butyl group is irradiated for **a**.

(8) All new compounds cited in this article gave satisfactory spectral data and elemental analyses (or exact mass).

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(10) We have not conclusively established which benzylic position is allylated. Both 1,11-transannular H-atom abstraction and analogous 1,8-processes are possible.

(11) A mixture of methyl acrylate telomers ($n = 1$–6) showed no change in distribution after being subjected to conditions used in workup.

(12) The macrocycle analogous to **4** formed in the reaction of **2a** (R_3 = *t*-Bu) was isolated in 60% yield under identical conditions to those that give the histogram shown in Figure 2b. The product **6** ($n = 2$, R = allyl) formed under our standard conditions was isolated from one reaction of template **2a** (R_3 = *t*-Bu) in 30% yield for the three-step sequence involving template reaction, hydrolysis of auxiliary, and conversion to the methyl ester.

and M. Kottenhahn, Forschung Chemie-Organische und Biologische Chemie, Degussa AG, for a sample of L-*tert*-butylleucine.

Supplementary Material Available: Details for the synthesis of representative templates, procedures for carrying out the addition/cyclization/transfer reaction, and analysis of telomers **6** (5 pages). Ordering information is available on any current masthead page.

Neighboring Group Activation of Acetal Cleavage: A Novel Nonacidic Strategy for the Tandem Formation of Cyclic Ethers

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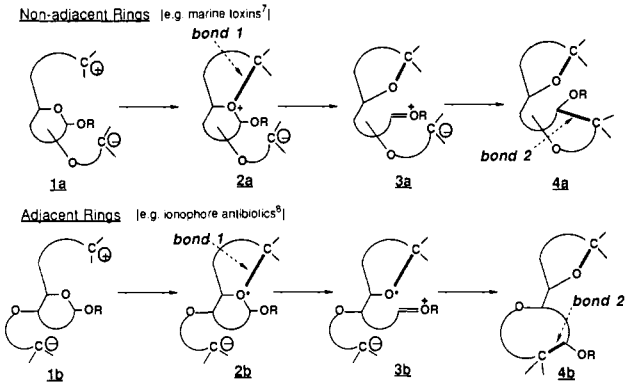
Synthetic approaches to complex polycyclic ethers invariably result in circuitous strategies in order to facilitate alcohol differentiation in polyol precursors. In this vein, carbohydrate-based approaches[1] have been popular because of the distinct reactivities of the hydroxy groups in monosaccharides.[2] Furthermore the cyclic acetal residue represents a masked hydroxy aldehyde, the elaboration of which may be strategically timed. With these considerations in mind, we envisaged a novel, tandem strategy for preparation of complex polyethers, which involves the sequencing of two different[3] ether-forming reactions on a monosaccharide template: (i) initial ether formation resulting from the attack of the ring oxygen on a remote electrophilic center, thereby leading to formation of an intermediate oxonium ion **2**, which undergoes cleavage of the internal C–O bond of the acetal to give the cyclic ether–oxocarbenium ion **3**,[4] followed by (ii) the intramolecular trapping of **3** by a carbon nucleophile[5,6] tethered to one of the hydroxy groups on the sugar. In this way adjacent and nonadjacent, bis-cyclic ether frameworks of varying ring sizes, related to important naturally occurring polyethers,[7,8] may be obtained by changing the location of the electrophile and nucleophile on different monosaccharide templates (Scheme I).

For the initial evaluation of the strategy, the alkenes **6** and **10** were prepared in three straightforward steps from the known carbohydrate building blocks **5**[9] and **9**[10] via selective formation

Scheme I



of the primary iodide,[11] followed by the Keck allyl radical coupling procedure[12] and O-alkylation of the remaining alcohol with 3-methoxybenzyl chloride or isoprenyl bromide (Scheme II).

Treatment of **6** and **10** with iodonium dicollidine perchlorate[4,13] (IDCP) in anhydrous dichloromethane under high-dilution conditions[14] (0.01 M), at room temperature, led within 10 and 45 min, respectively, to C1 epimeric pairs **7a** (60%) and **7b** (30%), each as a 6/5, cis/trans, THF (ring A) mixture, and **11** (93%), as a 5/3, cis/trans, ring A mixture. As expected from previous studies on 5-alkoxyalkenes, in neither case was THP formation observed in the initial halocyclization reaction.[15] Stereochemical assignments in the THF residues were made from comparison of ^{13}C chemical shifts in closely related compounds.[16] The structures of the cyclization products were verified, and the diastereomer composition for the THPs (ring B) was determined by conversion under zinc-mediated reductive elimination reaction conditions to the respective hydroxyalkenes, which were characterized as the acetate derivatives **8a/b** and **12**.

The ability to effect THP, in addition to THF, formation in the first stage of the reaction significantly increases the versatility of the methodology. This scenario requires an RO6 triggered reaction, and in order to test the feasibility of this plan, the homologous derivatives **13** and **16** were prepared from a three-step hydroboration–oxidation–methylenation sequence on the RO5 precursors, **6** and **10**. Application of the standard cyclization conditions led to bis-THP mixtures **14a/b** and **17** in 70 and 89% yields, after 16 h and 45 min, respectively. The stereochemistry of the initially formed THP in **17** was assignd by careful analysis of the ^1H NMR spectrum of the major isomer, and that for **14** was deduced from comparison of the ^{13}C NMR chemical shifts of the two compounds. Not surprisingly, the stereoselectivities in the formation of ring B for both RO5 and RO6 triggered reactions were similar. In particular, the reactions of the 1,2-*O*-isopropylidene substrates which afforded a single, ring B diastereomer are noteworthy. This result presumably reflects the stereochemical bias of nucleophilic addition to the intermediate cyclic oxocarbenium species.

These results indicate that the triggering RO5 and RO6 participation reactions were highly efficient in both the pyranoside

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(14) At higher concentrations, significant proportions of the aldehyde products were observed, presumably resulting from hydrolysis of the collidinium acetal which would have arisen from the intermolecular capture of the intermediate oxocarbenium ion by the collidine ligand in the reagent.

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(16) The resonances for the methylene carbons of the cis THF were observed to be consistently upfield relative to those of the trans isomer in related compounds whose structures were verified by degradation to both diastereomers of 5-methyltetrahydrofuran-2-methanol.[17]

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