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[17] This hypothesis relies on several reactions involving the Hoffmann test as well as MO calculations and will be discussed in detail in due course.

[18] All complexes formed from the carbanions and the chiral ligands were soluble in cumene.

Hydroxy-Directed, SmI$_2$-Induced Conversion of Carbohydrates into Carbocycles**

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Recently, we established that the configuration of the hydroxy groups in a starting material has a powerful influence in facilitating the reductive couplings promoted by samarium(II) iodide[1] and in controlling the stereochemical outcome.[2, 3] All of these hydroxy-directed carbon–carbon bond formation reactions proceed in good yields and provide access to highly funtionalized molecules with excellent stereocontrol. Furthermore, the sense of the diastereoselectivity was in full accordance with a chelation-control model. We have now discovered that this new methodology allows the stereoselective construction of polyoxygenated six-membered carbocycles from carbohydrate templates. During the last decade, organic chemists have been very interested in the transformation of carbohydrates to carbocycles.[4] Although most current approaches involve a radical methodology, only a limited number of SmI$_2$-mediated annulations of five-membered ring carbocycles from carbohydrates have been reported.[5]

As shown in Scheme 1, the six-membered ring carbocycles can be accessed from the allyl sulfides **1** and **4**, which are prepared from methyl β-D-glucopyranoside and β-D-galactopyranoside by simple carbohydrate manipulations.[6] When **1** was allowed to react directly with SmI$_2$ (2.5 equiv) at room temperature in THF/MeOH (5/1), the ring-closing reaction proceeded with complete stereochemical control to furnish the *cis*-1,3-cyclohexanediols **2** and **3** in a 75:25 ratio and in excellent yield. Similarly, the *cis*-1,3-cyclohexanediols **5** and **6** (27:73) were exclusively obtained through the SmI$_2$-mediated reaction of **4**.[9] Apparently, the corresponding δ-hydroxy aldehydes **7** and **8** must be generated in equilibrium processes before the self-terminating 6-*exo-trig* ketyl–olefin cyclization mediated by SmI$_2$ (Scheme 2).[10] This new annulation process is of considerable synthetic utility not only because of the observed high diastereoselectivity but also because of the exceptional synthetic versatility of the cyclization products.

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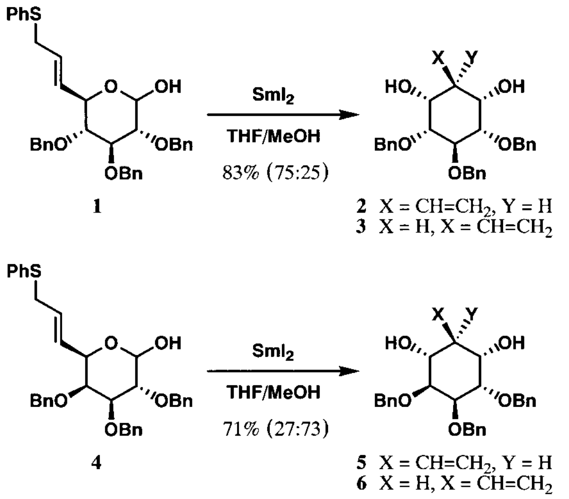
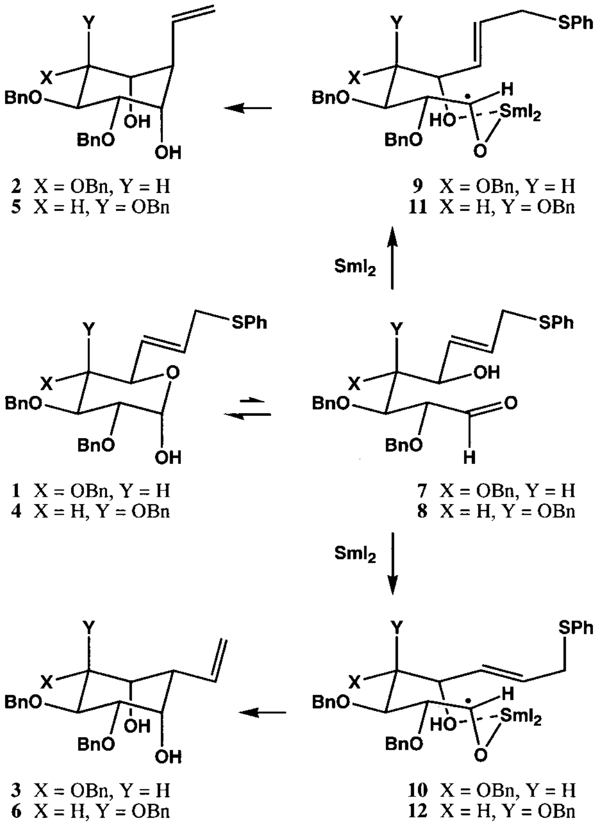


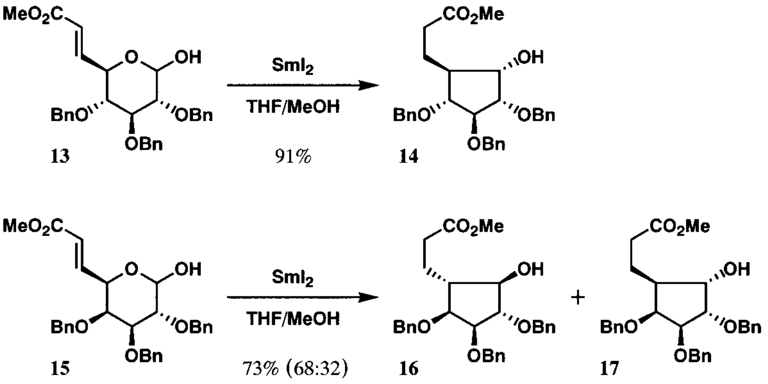
Scheme 1. Cyclizations to form six-membered rings. Bn = benzyl.



Scheme 2. The chelation-control model.

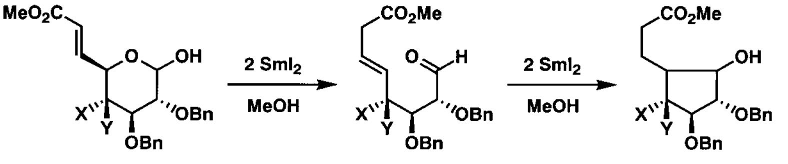
In the cyclization products **2**, **3**, **5**, and **6**, the two hydroxy groups are situated *cis* on the new six-membered rings (Scheme 2). Thus, the high stereoselectivity can be again explained by assuming a chelation-control model.[2] After the single-electron reduction of the aldehyde part of **7** or **8**, chelation of the Sm^{III} cation attached to the resulting ketyl radical with the δ-hydroxy group of **7** or **8** gives the requisite species for the construction of the cyclic ketyl intermediate. The ketyl radical center adds to the olefinic part through the plausible transition states **9** and **10** or **11** and **12**. The β-scission reaction of the cyclic radical intermediates with a second equivalent of SmI_2 in turn leads to the *cis*-1,3-cyclohexanediol products **2** and **3** or **5** and **6**, respectively.

In stark contrast, the five-membered ring carbocycles were constructed with complete chemoselectivity through a similar SmI_2-induced cyclization of the corresponding α,β-unsaturated methyl esters **13** and **15** (Scheme 3).[6] Direct treatment of **13** with SmI_2 (5.0 equiv) at 0 °C in THF/MeOH (15/1) provided the cyclopentanol **14** as the sole product in excellent yield. The same cyclization of **15** affected exclusive formation of the cyclopentanols **16** and **17** (68:32).[9]



Scheme 3. Cyclizations to form five-membered rings.

When 2.5 equiv of SmI_2 are added to **13** at −40 °C in THF/MeOH (15/1), the β,γ-unsaturated methyl ester **18** was obtained (Scheme 4). Furthermore, coupling cyclization of **18** with 2.5 equiv of SmI_2 at 0 °C in THF/MeOH (15/1) produced **14** as a single stereoisomer in 87 % yield. Therefore, the SmI_2-mediated reductive cyclizations of **13** and **15** may involve sequential ring-opening and ketyl–olefin annulation reactions. Thus, the ring-cleavage reactions of tetrahydropyran with SmI_2 are initiated by the single-electron reduction of the α,β-unsaturated ester moiety of **13** or **15**, forming the intermediate β,γ-unsaturated methyl ester **18** or **19**.[11] The SmI_2-promoted 5-*exo-trig* ketyl–olefin cyclization of **18** or **19** generated in situ affords the observed cyclopentanol products **14** or **16** and **17**, respectively.



Scheme 4. The pathway involving ring opening and ketyl–olefin coupling.

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Luminescence of Novel Neodymium Sulfonylaminate Complexes in Organic Media[**]

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Neodymium(III)-containing solids are the most popular luminescent materials for application in laser systems.[1] Inorganic Nd^{III} compounds such as oxides, fluorides, phosphates, and their mixed matrices were investigated for the capability of high power laser radiation by controlling the Nd^{III} density in matrices. The construction of strongly luminescent Nd^{III} materials in organic media would be desirable for developing applications in novel organic Nd^{III} devices, such as organic liquid lasers, optical-fiber polymers, organic electroluminescent devices, and near-IR immunoassays.[2] However, the energy gap theory shows that the presence of C–H or O–H bonds in the vicinity of Nd^{III} leads to effective radiationless transitions by vibrational excitation of C–H or O–H bonds, and this results in negligible emission quantum yields.[3] Suppression of such vibrational excitation in the Nd^{III} system requires deuteration of C–H and O–H bonds or replacement of C–H bonds with C–F bonds in ligating molecules, and the use of deuterated solvents with low vibrational frequencies. By using these strategies, various researchers recently observed effective emission in certain organic/Nd^{III} systems.[4] However, an emission quantum yield on the order of 10^{-5} was never observed in solvents that contain H atoms. Here we report on the luminescence of novel Nd^{III} complexes and the first observation of enhanced luminescence of Nd^{III} in a solvent of high vibrational frequency, namely, undeuterated acetone, by using bis(perfluoroalkylsulfonyl)aminates as bulky ligands with low vibrational frequencies.

Bis(perfluorooctylsulfonyl)amine (posH) was synthesized by treating the corresponding perfluorooctylsulfonylamine with perfluorooctylsulfonyl fluoride in the presence of triethylamine (TEA) as base in THF, followed by acidification with 10% aqueous H_2SO_4. $[Nd(pos)_3]$ was prepared by treating posH with neodymium oxide in water. For comparison, we prepared $[Nd(pbs)_3]$ (pbs = bis-perfluorobutylsulfo-

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