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

Hydroxy-Directed, SmI₂-Induced Conversion of Carbohydrates into Carbocycles**

Toshiyuki Kan, Shinji Nara, Takashi Ozawa, Haruhisa Shirahama, and Fuyuhiko Matsuda*

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 functionalized 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 SmI₂-mediated annulations of five-membered ring carbocycles from carbohydrates have been reported.^[5]

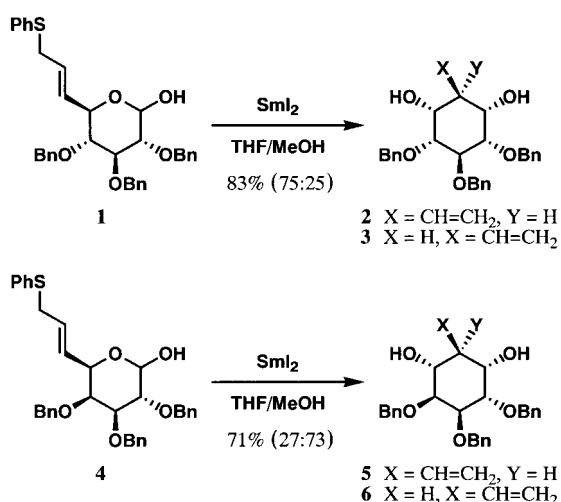
As shown in Scheme 1, the six-membered ring carbocycles can be accessed from the allyl sulfides **1** and **4**, which are prepared from methyl β -D-glucopyranoside and β -D-galactopyranoside by simple carbohydrate manipulations.^[6] When **1** was allowed to react directly with SmI₂ (2.5 equiv) at room 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 SmI₂-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 SmI₂ (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.

[*] Prof. Dr. F. Matsuda,^[+] Dr. T. Kan, Dr. S. Nara, T. Ozawa, Prof. Dr. H. Shirahama
Department of Chemistry, Faculty of Science
Hokkaido University
Sapporo 060-0810 (Japan)
E-mail: fmatsuda@ees.hokudai.ac.jp

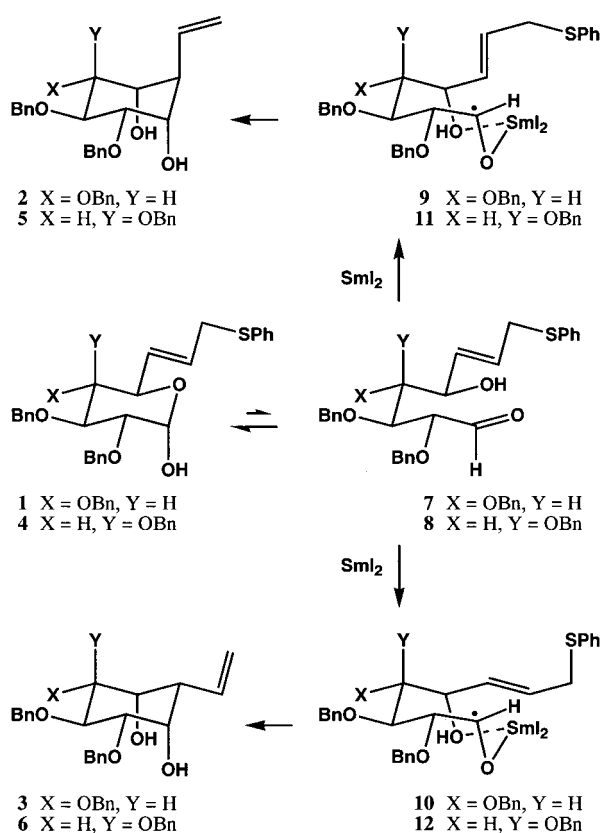
[+] Current address:
Division of Material Science
Graduate School of Environmental Earth Science
Hokkaido University
Sapporo 060-0810 (Japan)
Fax: (+81)11757-5995

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

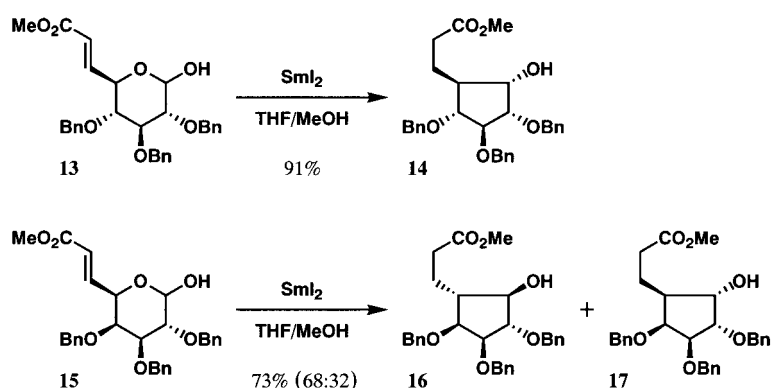


Scheme 2. The chelation-control model.

In the cyclization products **2**, **3**, **5**, and **6**, the two hydroxy groups are situated *cis* to 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 SmI₂ in turn leads to the *cis*-1,3-cyclohexanediol products **2** and **3** or **5** and **6**, respectively.

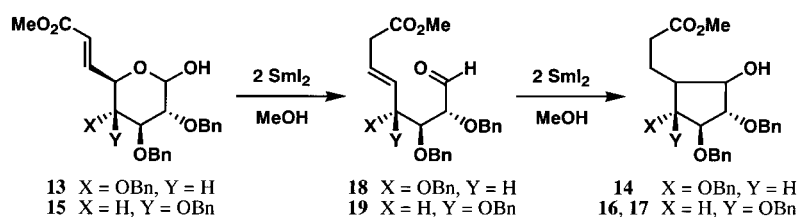
In stark contrast, the five-membered ring carbocycles were constructed with complete chemoselectivity through a similar SmI₂-induced cyclization of the corresponding α,β -unsaturated methyl esters **13** and **15** (Scheme 3).^[6] Direct treatment



Scheme 3. Cyclizations to form five-membered rings.

of **13** with SmI₂ (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 cyclopentanol **16** and **17** (68:32).^[9]

When 2.5 equiv of SmI₂ 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



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

18 with 2.5 equiv of SmI₂ at 0 °C in THF/MeOH (15/1) produced **14** as a single stereoisomer in 87 % yield. Therefore, the SmI₂-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 SmI₂ 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 SmI₂-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.

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Luminescence of Novel Neodymium Sulfonylamine Complexes in Organic Media**

Yasuchika Hasegawa, Takashi Ohkubo, Kensaku Sogabe, Yuichiro Kawamura, Yuji Wada, Nobuaki Nakashima, and Shozo Yanagida*

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)amines 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 H₂SO₄. [Nd(pos)₃] was prepared by treating posH with neodymium oxide in water. For comparison, we prepared [Nd(pbs)₃] (pbs = bis-perfluorobutylsulfo-

[*] Prof. S. Yanagida, Y. Hasegawa, T. Ohkubo, Y. Kawamura, Y. Wada
Material and Life Science, Graduate School of Engineering
Osaka University
Yamada-oka, Suita, Osaka 565-0871 (Japan)
Fax: (+81)6-6879-7875
E-mail: yanagida@chem.eng.osaka-u.ac.jp
Prof. N. Nakashima
Department of Chemistry, Faculty of Science
Osaka City University
Osaka, Osaka 558 (Japan)

K. Sogabe
New Development Division, New Japan Chemical Co., Ltd.
Yoshijima 13, Yagura-cho, Fushimi-ku, Kyoto 612-8224 (Japan)

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