Recent Advances in the Conversion of Carbohydrate Furanosides and Pyranosides into Carbocycles

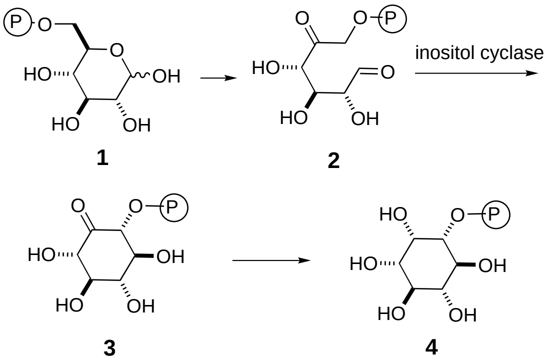
Peter I. Dalko* and Pierre Sinaÿ*

In memory of Stéphan D. Géro

Carbocyclic polyols are important constituents of many biologically active molecules. They exhibit far-reaching biological effects, ranging from cellular regulation to the selective inhibition of enzymes which play key roles in living organisms.[1, 2] They may be divided into two categories, those containing six- and those containing five-membered carbon rings. Among the most prominent of the six-membered representatives are cyclohexane hexitols, such as inositol derivatives,[1b] and pseudosugars,[1f, 2, 3] such as cyclophellitol[4] and valienamine.[5] Structural analogues of the latter are constituents of compounds of key pharmacological interest, for example acarbose,[6] adiposin,[7] trestatin,[8] and amylostatin.[9] Together with a growing number of structurally related alkaloids,[10] purely synthetic analogues,[11] and natural products containing five-membered polyols,[12, 13] these small but synthetically challenging molecules have received growing interest in the last few years.

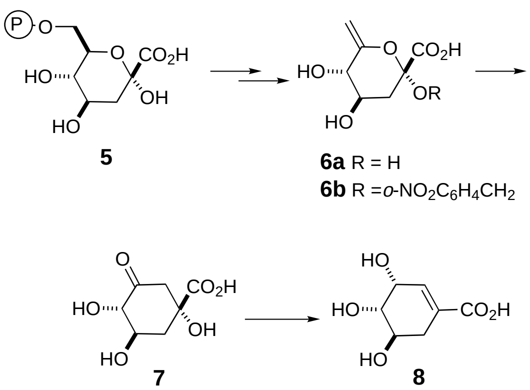
Owing to their biological significance and the inherent structural challenge they present, a variety of different approaches to obtain optically pure carbocyclic polyols has been developed.[14] These strategies include 1) cyclization of alicyclic, polyfunctionalized molecules and 2) transformations of conveniently substituted carbocycles. Included in the first strategy are cycloaddition reactions,[15] Wittig-type olefinations,[16] radical cyclization approaches[17] including reductive couplings,[18] ring-closing methathesis (RCM),[19] and a variety of anionic[14] or transition metal mediated[20] cyclization reactions of advanced polyhydroxylated compounds. Historically, a tandem fragmentation/Henry-type cyclization reaction provided the first examples in which cyclohexane[21] and cyclopentane derivatives[22] were obtained from a carbohydrate. An elegant application of the Fujimoto–Belleau reaction by Vasella et al.[23] and the anionic rearrangement of anhydrosugars[24] are also examples of this strategy. Some of the above transformations allow the direct conversion of carbohydrate furanosides and pyranosides into carbocyclic polyols. Strategies which include enantiopure carbocycles as starting materials feature transformations of quinic acid,[25] inositols, or conduritol derivatives;[26] desymmetrization of *meso* cyclohexene derivatives by asymmetric palladium catalyzed hydroxycarboxylation;[27] enantioselective alkylation;[28] and transformation of homochiral carbocycles either by microbial[29, 30] or chemical oxidation.[28, 31]

Somewhat surprisingly, the biosynthesis of the carbocyclic polyols is not thoroughly understood, probably because their biogenesis does not follow a general, unified path. It has been found that *myo*-inositol derivatives, for example, are formed from D-glucose 6-phosphate (**1**) by stereospecific ring closure under the catalytic influence of inositol cyclase (Scheme 1).[1b]



Scheme 1. Synthesis of *myo*-inositol 1-phosphate (**4**) from **1** under the catalytic influence of inositol cyclase. Ⓟ = phosphate.

Other biosyntheses bear strong resemblances to the mechanism by which D-glucose is converted into shikimic acid (**8**; Scheme 2). This is the biogenetic path in which nature produces the benzoid rings of the aromatic amino acids and an extensive range of other metabolites. At an early stage of this sequence the hemiacetal intermediate **6a** undergoes rearrangement and forms the quinic acid derivative 3-dehydroquinic acid (**7**). However, Bartlett and Satake demon-



Scheme 2. Biogenetic synthesis of shikimic acid (**8**).

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[*] Dr. P. I. Dalko
Laboratoire de Synthèse des Substances Naturelles
associé au CNRS
Bât 410, F-91405 Orsay Cédex (France)
Fax: (+33) 1-69-15-46-79
E-mail: petdalko@icmo.u-psud.fr

Prof. Dr. P. Sinaÿ
Ecole Normale Supérieure
Département de Chimie, associé au CNRS
24 rue Lhomond, F-75231 Paris Cédex 05 (France)
Fax: (+33) 1-44-32-33-90
E-mail: pierre.sinay@ens.fr

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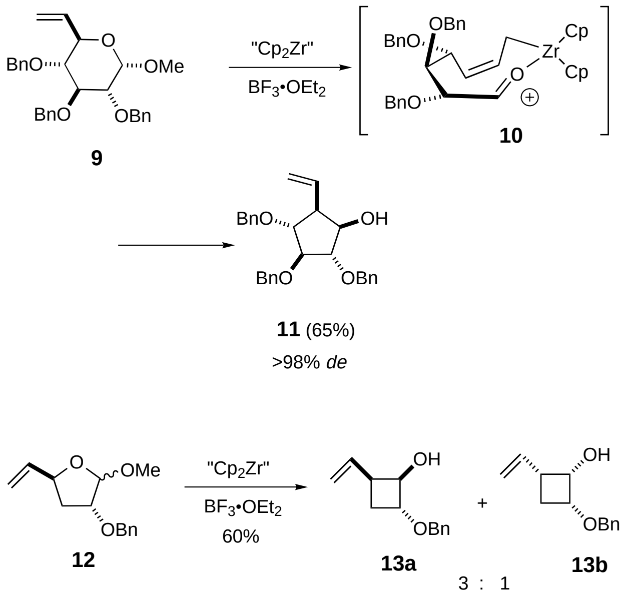
strated that the unstable **6a**, generated in situ from the *o*-nitrobenzyl-protected α-glycoside **6b**, rearranges spontaneously to **7** in the absence of a specific enzyme.[32] Moreover, this uncatalyzed reaction gives rise to a single stereoisomer, identical to that of the biosynthetic path. This fact suggests that cyclitol biosynthesis may also be nonenzymatic.

Nature has found a direct way to perform this tandem fragmentation cyclization reaction in a stereospecific manner and under neutral conditions. Human creativity and good luck have uncovered synthetic strategies which can compete efficiently with nature. With the advent of mild, metal-mediated cyclization reactions, the early work of Grosheinz and Fischer,[21] who converted 6-deoxy-6-nitrohexoses into nitroinositols in a single step, matured to a general strategy of broad interest. The methods that have been used include 1) the ring contraction of carbohydrate derivatives[33] into functionalized cyclopentanes and cyclobutanes and 2) the conversion of a variety of sugar furanosides and pyranosides into highly functionalized carbocyclic derivatives of five and six carbon atoms, respectively.

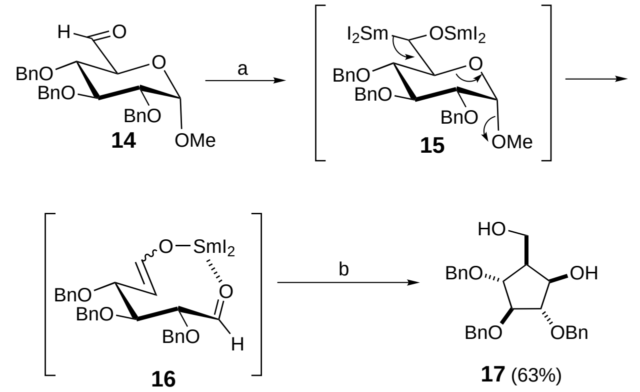
Ring Contraction of Carbohydrate Derivatives

Vinyl carbohydrate derivatives **9** or **12** can be converted into carbocycles **11** and **13** respectively by sequential treatment with "Cp_2Zr" ($Cp = C_5H_5$) and $BF_3 \cdot OEt_2$ (Scheme 3).[34] The reaction selectively forms the product in which the vinyl group is *cis* to the newly formed hydroxyl group. Although the major stereoisomer was expected to show a *trans* orientation of the vinyl group with respect to the adjacent α substituent, the overall selectivity of the reaction depends intimately on the stereochemistry and nature of the substituents present. Despite the difficulty encountered with different derivatives in controlling stereochemistry, the easy access and the seemingly unhindered choice of the vinyl carbohydrate starting materials renders this methodology appealing.

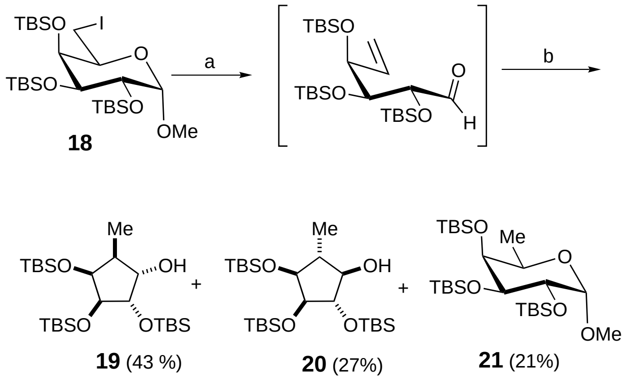


Scheme 3. Synthesis of carbocycles **11** and **13** from vinyl carbohydrate derivatives **9** and **12**. Bn = benzyl.

Samarium(II) iodide promotes a comparable transformation of aldehyde **14** to ring-contracted product **17** (Scheme 4).[35] The presence of HMPA and *tert*-butyl alcohol as a proton source is necessary to obtain a good conversion into the cyclopentane derivative. The reaction is considered to proceed via the samarium ketyl intermediate, which is reduced to the disamarium species **15** under the reaction conditions. After fragmentation, the system is ideally set up for a subsequent aldol cyclization, involving intramolecular nucleophilic attack of the samarium enolate onto the aldehyde through a 5-enol *exo-exo-trig* process. As expected from a metal-linked chelate, the major stereoisomer is that in which the two newly created stereocenters are *cis* with respect to one another and *trans* with respect to the adjacent substituents.



Scheme 4. Synthesis of **17** from aldehyde **14**. a) SmI_2, THF, hexamethyl phosphoramide (HMPA); b) SmI_2, THF, HMPA, *t*BuOH (2 equiv).

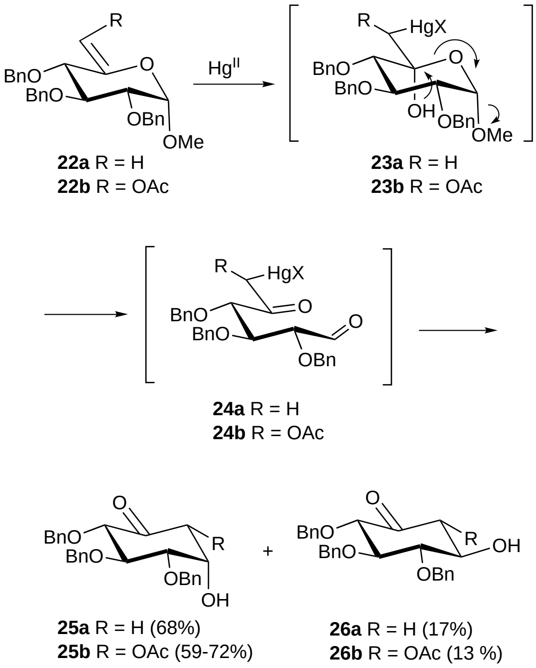


Scheme 5. The SmI_2-promoted ring-contraction reaction of **18** to provide **19**–**21**. a) SmI_2, THF, HMPA; b) SmI_2, THF, HMPA, then H^+. TBS = *tert*-butyldimethylsilyl.

A similar reductive ketyl–olefine coupling is hypothesized as the key cyclization step in the SmI_2-promoted ring contraction of 6-deoxy-6-iodohexopyranosides[36a] such as **18** (Scheme 5). This sequence requires four single electron transfer (SET) steps (i.e., at least 4 molequiv of SmI_2 are necessary to complete the reaction) and consist of 1) reductive dealkoxyhalogenation to give the ring-opened hex-5-enal, 2) an intramolecular ketyl–olefin reductive coupling to afford the ring-contracted organosamarium intermediate, and 3) the intermolecular trapping of this intermediate to produce branched cyclopentitol derivatives such as **19** and **20**. The cyclopentane products were isolated along with the corresponding 6-deoxypyranoside **21**. In cases where cyclization occurred, the major products usually had a relative *trans* configuration between the newly formed methyl group and the hydroxyl group. In addition, a *trans* orientation between the hydroxyl group and the vicinal alkoxy group was observed.[36b]

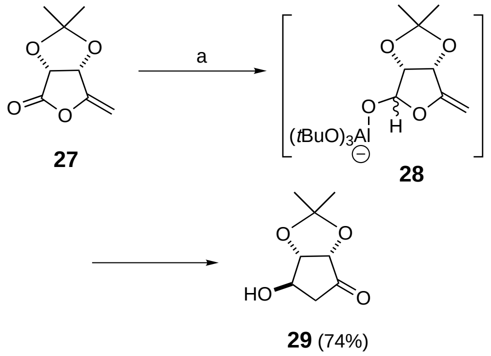
Conversion of Sugar Furanosides and Pyranosides into Highly Functionalized Carbocyclic Derivatives

Sugar enol-ethers which inherently carry both masked nucleophilic and electrophilic functionalities have been converted into carbocycles. The first breakthrough for this class of reaction was the mercury(II)-mediated rearrangement of hex-5-enopyranoside derivatives, generally termed the Ferrier (II) reaction.[37] For example **22a** gives the highly functionalized cyclohexanones **25a** and **26a** (Scheme 6). This remarkable reaction has provided a practical route to a large variety of bioactive substances such as aminocyclitols,[38] pseudosugars,[39] inositols,[40] and other complex hexitols.[41] Among the various conditions empoyed for the Ferrier (II) reaction, both catalytic and stoichiometric methods have been investigated. These afford similar but not identical results.[14, 42] Also, a "nontoxic alternative" makes use of a catalytic amount of palladium(II) instead of mercury(II).[43] This modification can slightly alter the selectivity, which is not surprising given the different coordination pattern of the metal center in the transition state. The basic features of this transformation are the loss of the glycosidic functionality, for example as methanol by fragmentation, and the ring-closing aldol reaction. In this cyclization the carbanionic center (C6) attacks the electrophilic carbonyl center (C1). The stereochemistry of the newly formed asymmetric center is influenced by the conformational bias of the molecule, the chemical nature of the functionalities present, and the reaction conditions. Yields of isolated products are also highly dependent upon the experimental conditions. These observations are thought to be due to the preferred conformation of the given sugar derivative in the transition state and to the possibility of formation of a sensitive β-hydroxy ketone, which can undergo elimination and subsequent aromatization. The scope of the reaction was enlarged by the demonstration that functionalized exocyclic olefins may be converted into carbocycles as well. For example, **22b**, made from the corresponding aldehyde, was transformed to inosose derivative **25b** with high stereoselectivity of each newly formed stereogenic center (Scheme 6).



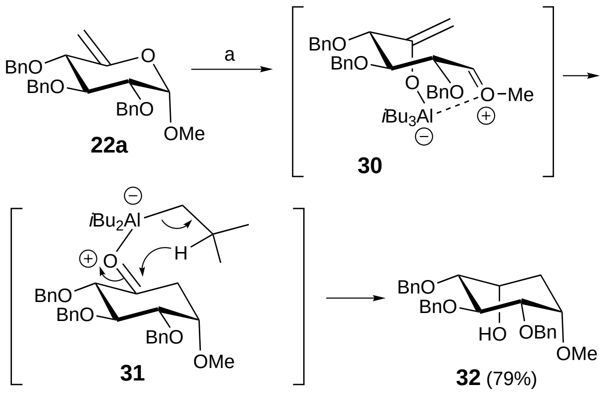
Scheme 6. Synthesis of functionalized cyclohexanones **25** and **26** from **22**.

The Ferrier (II) reaction is a quite efficient way to form six-membered carbocycles, but is unsuitable to transform furanosides to cyclopentitols. Subtle changes in the transition state conformation and complexation patterns prevent carbocyclization. The solution for this challenging problem was uncovered with an aluminium hydride based Lewis acid. Five-membered enollactone **27** was converted into the cyclopentanone derivative **29** as a single epimer upon treatment by LiAlH(O*t*Bu)$_3$ (Scheme 7).[44] Spectroscopic studies have established some mechanistic details. Hydride adds rapidly to the carbonyl, and a stable aluminate complex is formed. The carbocyclization occurs by protonation followed by fragmentation and an aldol-type cyclization process.



Scheme 7. Rearrangement of the enollactone **27** to a cyclopentanone derivative **29**. a) LiAlH(O*t*Bu)$_3$, THF, 0 °C, then NH$_4$Cl (aq.).

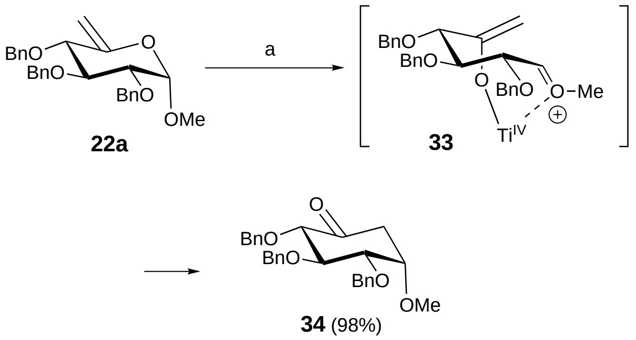
Under the particularly mild conditions of a triisobutylaluminium-mediated rearrangement the fragmentation of the "locked" anomeric substituent in **22a** was avoided. Retention of configuration with high selectivity was observed.[45] Lewis acid assisted *endo* activation, followed by a ring-opening step, is hypothesized to generate the zwitterionic enolate **30** (Scheme 8). Ring closure is thought to occur by an intramolecular 6-*exo-trig* aldol condensation. The "bonus" of the reaction is the stereoselective formation of a hydroxyl group, resulting from the final reduction of the keto group, probably by intramolecular hydrogen delivery from the less hindered β side. The reaction is fairly general and high-yielding; a wide



Scheme 8. Synthesis of **32** from **22a** via the zwitterionic enolate **30**. a) $i\mathrm{Bu_3Al}$, toluene, 40 °C.

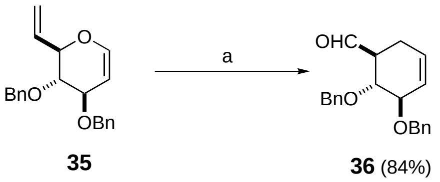
array of sugar starting materials have been used. The good selectivity in conserving the anomeric stereochemical information is worth noting. The reaction proceeds with retention of configuration.

A similar strategy was developed with titanium(IV) derivatives as Lewis acids.[46] In the presence of $[\mathrm{TiCl_3}(\mathrm{O}i\mathrm{Pr})]$ the α-D-glycoside **22a** undergoes the expected *endo* cleavage of the glycosidic bond and forms the carbocyclic glycoside **34** with retention of configuration at the former anomeric center (Scheme 9). Although the reaction of the α-glycoside proceeds in nearly quantitative yield, the corresponding β-glycoside gives rise to a mixture of different products. The titanium(IV) reaction is even milder than the triisobutylaluminium-mediated rearrangement and does not result in reduction of the keto functionality.



Scheme 9. Synthesis of carbocyclic glycoside **34** from **22a**. a) $[\mathrm{TiCl_3}(\mathrm{O}i\mathrm{Pr})]$ (1.5 equiv), $\mathrm{CH_2Cl_2}$, −78 °C, 15 min.

Pseudosugars have been prepared by an elegant thermal [3,3] sigmatropic rearrangement.[47] This methodology, which is conceptually different from the fragmentation/cyclization strategy discussed above, is based on the work of Büchi and Powell.[48] Although the generality of this approach using different sugar series remains to be demonstrated, the simplicity is attractive. Vinyl glucal derivative **35** affords the cyclohexene aldehyde **37** on heating (Scheme 10). One of the advantage of this transformation is that the pseudosugar formed retains the original configuration of the starting sugar. D-Glucal derivatives give entry to the pseudo-D-glucal series.



Scheme 10. Synthesis of cyclohexene aldehyde **36** from vinyl glucal derivative **35**. a) 240 °C, *o*-dichlorobenzene, sealed tube, 1 h.

Conclusion

The access of enantiomerically pure carbocyclic polyols from carbohydrate furanosides and pyranosides is an attractive proposition. New methods have made it possible to carry out such transformations under mild conditions in good yields and with high, predictable stereoselectivity. Their compatibility with a large variety of substituents gives the discussed rearrangements strategical importance.

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