Heterocycles

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Synthesis of Enantiopure Carbohydrate Mimetics by Lewis Acid Catalyzed Rearrangement of 1,3-Dioxolanyl-Substituted 1,2-Oxazines**

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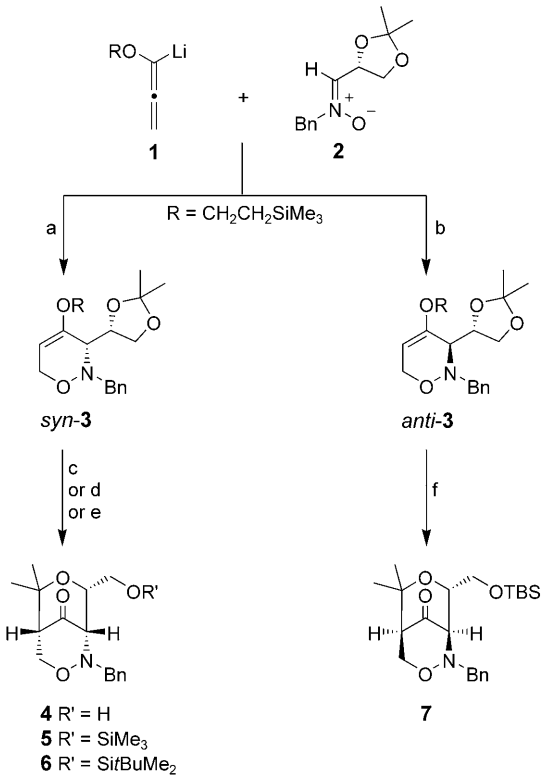
Dedicated to Professor Helmut Vorbrüggen on the occasion of his 75th birthday

Enantiomerically pure 3,6-dihydro-2*H*-1,2-oxazines, which are easily available by [3+3] cyclization of lithiated alkoxyallenes with aldonitrones,[1] are versatile intermediates for the stereoselective synthesis of a range of highly functionalized compounds. All these products, including polyhydroxylated pyrrolidines, stereodefined amino polyols, and substituted tetrahydrofuran derivatives,[2] are interesting because of their potential biological activities, for example, as glycosidase inhibitors.[3] While trying to deprotect 1,2-oxazine *syn*-**3** with Lewis acids we found that a rearrangement to tetrahydropyran-bridged bicyclic 1,2-oxazine **4** occurred in moderate yield (Scheme 1).[2b] Thereby the acetonide protecting group of *syn*-**3** was incorporated into product **4**. Herein we report that:

- this reaction proceeds quite generally with suitably substituted 3,6-dihydro-2*H*-1,2-oxazines as starting materials,
- the obtained enantiopure bicyclic products can be converted stereoselectively into numerous polyhydroxylated amino-substituted pyran derivatives,
- in a similar manner, highly functionalized oxepane derivatives are accessible.

The resulting products may be regarded as carbohydrate mimetics,[4] which are potentially important building blocks for the synthesis of biologically active compounds, for example, oligosaccharide analogues.

The stereodivergent addition of lithiated alkoxyallene **1** to the D-glyceraldehyde-derived nitrone **2** gives either *syn*- or *anti*-configured **3** in excellent yield (Scheme 1).[1] The unexpected cyclization of *syn*-**3** to **4**, which was first observed in moderate yields in the presence of $BF_3{\cdot}OEt_2$, was optimized by using a range of Lewis acids and screening the reaction conditions. Although the rearrangement could be accomplished with different Lewis acids, dibutylboron triflate, trimethylsilyl triflate, and tin tetrachloride proved to be the best promoters.[5] The conversion of *syn*-**3** into bicyclic product **4** proceeded quantitatively with $SnCl_4$ in acetonitrile.



Scheme 1. Reaction conditions: a) THF, −78 °C, 2 h (*syn*-**3**: 76%); b) **2** + Et_2AlCl, Et_2O, then add to **1**, −78 °C, 2 h (*anti*-**3**: 84%); c) $SnCl_4$ (3 equiv), CH_3CN, −30 °C→RT, 6 h (**4**: quant.); d) Me_3SiOTf (0.05 equiv), CH_2Cl_2, −30 °C→RT, 6 h (**5**: 79%); e) *t*$BuMe_2SiOTf$ (3 equiv), CH_2Cl_2, room temperature, 20 h, then NEt_3, 0 °C, 15 min (**6**: quant.); f) *t*$BuMe_2SiOTf$ (3 equiv), CH_2Cl_2, room temperature, 20 h, then NEt_3, 0 °C, 15 min (**7**: 93%). Bn = benzyl; TBS = *tert*-butyldimethylsilyl; Tf = trifluoromethanesulfonyl.

We propose that the mechanism of this reaction involves the coordination of the Lewis acid to the "outer" dioxolane oxygen atom (O-1) of *syn*-**3**, followed by ring opening of the acetonide unit and intramolecular attack of the generated carbenium ion at the enol ether unit of the 1,2-oxazine ring. Cleavage of the (trimethylsilyl)ethyl group—most probably to give ethene and Me_3SiX species[6]—affords the central carbonyl group of the resulting bicyclic compound **4**. This rearrangement can be classified as an intramolecular aldol-type addition of an acetal to an enol ether[7] or as a Prins reaction.[8]

The rearrangement can also be triggered by catalytic amounts of trimethylsilyl (TMS) triflate.[9] Treatment of *syn*-**3** with 0.05 equivalents of this mild Lewis acid led to TMS-protected derivative **5** in 79% yield. To introduce the more stable *tert*-butyldimethylsilyl protecting group, *syn*-**3** was treated with *t*$BuMe_2SiOTf$ (3 equiv) and then with triethyl-

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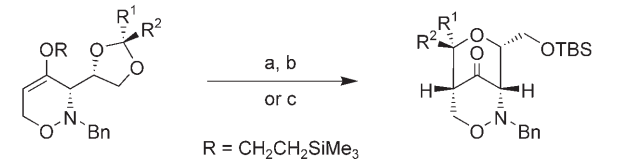
amine to generate bicyclic product **6**. In a similar manner the rearrangement of diastereomeric 1,2-oxazine *anti*-**3** led to protected bicyclic 1,2-oxazine **7** (Scheme 1). This compound can also be obtained by $SnCl_4$-induced rearrangement followed by silylation (80% yield). As diastereomeric heterocycles *syn*- and *anti*-**3** are enantiopure,[10] this should also hold for the corresponding bicyclic products **4**–**7**.

The incorporation of the acetonide unit into products **4**–**7** suggested that other "protecting" groups can be employed in the starting material to obtain differently substituted bicyclic compounds. Therefore *syn*-configured 1,2-oxazines **8**, **10**, and **12**, which contain cyclopentanone-, cyclohexanone-, and benzaldehyde-derived acetals, were synthesized in analogous procedures (Scheme 2).[11] As expected, treatment of **8** with



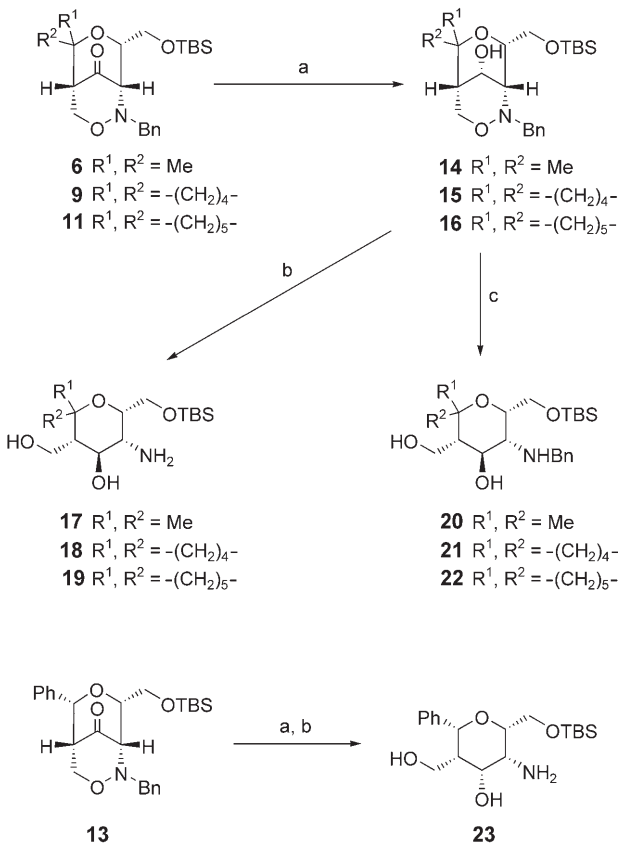
8 R^1, R^2 = -$(CH_2)_4$-
10 R^1, R^2 = -$(CH_2)_5$-
12 R^1 = Ph, R^2 = H

9 R^1, R^2 = -$(CH_2)_4$-
11 R^1, R^2 = -$(CH_2)_5$-
13 R^1 = Ph, R^2 = H

Scheme 2. Reaction conditions: a) $SnCl_4$ (3 equiv), CH_3CN, −30 °C → RT, 6 h; b) *t*$BuMe_2SiOTf$ (3 equiv), NEt_3, CH_2Cl_2, 0 °C, 1 h, (yields over two steps: **9**: 86%, **11**: 70%, **13**: 77%); c) *t*$BuMe_2SiOTf$ (3 equiv), CH_2Cl_2, room temperature, 20 h, then NEt_3, 0 °C, 15 min, (**11**, **13**: quant.).

tin tetrachloride followed by *O*-silylation gave spiro compound **9** in very good overall yield. For 1,2-oxazines **10** and **12** the one-step procedure with *tert*-butyldimethylsilyl triflate as promoter was chosen, leading directly to the protected rearrangement products **11** and **13** in excellent yields. The configuration at the acetal carbon atom of compound **12** did not affect the outcome: the pure *R*-configured bicyclic product **13** was obtained from both diastereoisomers (or a mixture of the two).[12] This can be expected if a carbenium ion with an equatorial aryl group is involved in the cyclization process. The *anti*-configured compounds underwent similarly efficient rearrangements.[5]

The bicyclic products presented contain an N−O bond whose cleavage should give access to highly functionalized enantiopure pyran derivatives. With ketones such as **6** this ring fission was not successful. However, after reduction of the carbonyl group of **6**, **9**, or **11** with $NaBH_4$ the resulting diastereomerically pure alcohols **14**–**16**, respectively (or their *O*-protected derivatives),[5] could be opened smoothly. Hydrogenolysis with hydrogen and palladium on charcoal did not only cleave the ring of the 1,2-oxazine but also removed the *N*-benzyl group to give primary amines **17**–**19** in good to very good yields (Scheme 3).[13] Debenzylation can be avoided by using the milder reducing agent samarium diiodide.[14] Secondary amines **20**–**22** were obtained after short reaction time in almost quantitative yields. These two reduction steps were used to convert phenyl-substituted bicyclic compound **13** into pyran derivative **23**, which contains five stereogenic centers.[15]



6 R^1, R^2 = Me
9 R^1, R^2 = -$(CH_2)_4$-
11 R^1, R^2 = -$(CH_2)_5$-

14 R^1, R^2 = Me
15 R^1, R^2 = -$(CH_2)_4$-
16 R^1, R^2 = -$(CH_2)_5$-

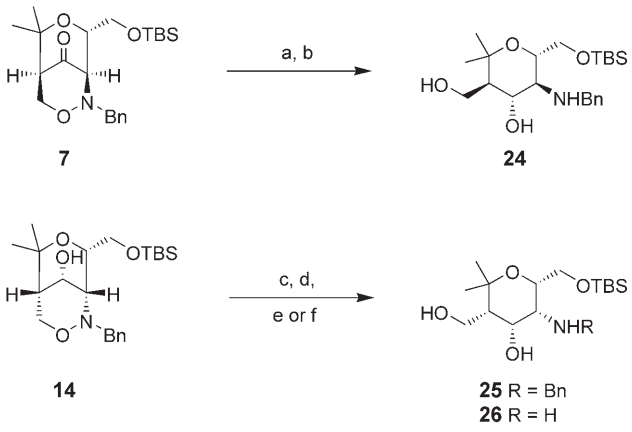
17 R^1, R^2 = Me
18 R^1, R^2 = -$(CH_2)_4$-
19 R^1, R^2 = -$(CH_2)_5$-

20 R^1, R^2 = Me
21 R^1, R^2 = -$(CH_2)_4$-
22 R^1, R^2 = -$(CH_2)_5$-

13 **23**

Scheme 3. Reaction conditions: a) $NaBH_4$, EtOH, 0 °C, 4 h, (**14**: 97%, **15**: 98%, **16**: 70%); b) H_2, Pd/C, MeOH, room temperature, 1 d, (**17**: 72%, **18**: 96%, **19**: 99%, **23**: 64% over two steps); c) SmI_2, THF, room temperature (**20**: quant., **21**: 93%, **22**: 95%).

Several options are available to generate different configurations of the tetrahydropyran derivatives. Bicyclic 1,2-oxazine **7** (derived from *anti*-**3**) was reduced with $NaBH_4$ and subsequent ring opening with samarium diiodide led to *trans*,*trans*,*trans*-**24** (Scheme 4). Hydrogenolysis gave the



7 **24**

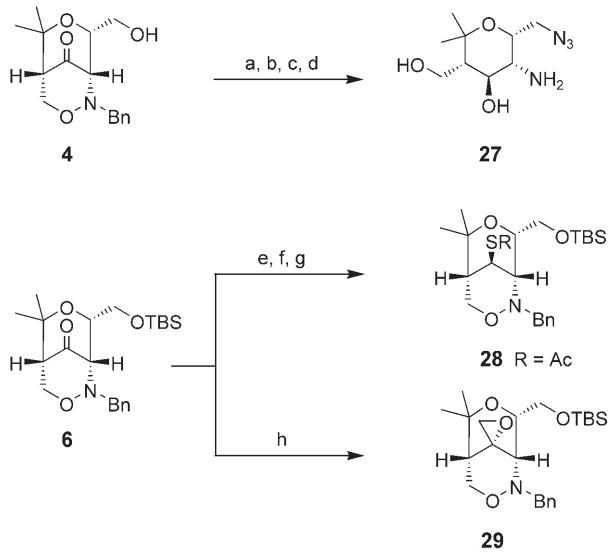
14

25 R = Bn
26 R = H

Scheme 4. Reaction conditions: a) $NaBH_4$, EtOH, 0 °C, 4 h (82%); b) SmI_2, THF, room temperature (72%); c) DEAD, PPh_3, *p*-nitrobenzoic acid, benzene, room temperature, 6 h, (81%); d) NaN_3, MeOH, 55 °C, 2 d, (78%); e) SmI_2, THF, room temperature (**25**: 81%); f) H_2, Pd/C, MeOH, room temperature (**26**: quant.). DEAD = diethylazodicarboxylate.

expected *N*-debenzylated product.[5] With bicyclic compound **14** as an example, it was demonstrated that Mitsunobu reaction[16] allows an inversion of configuration of the secondary hydroxy group and hence the synthesis of *all-cis*-substituted carbohydrate mimetics. Both methods of reduction provided the expected products **25** and **26** in good yields.

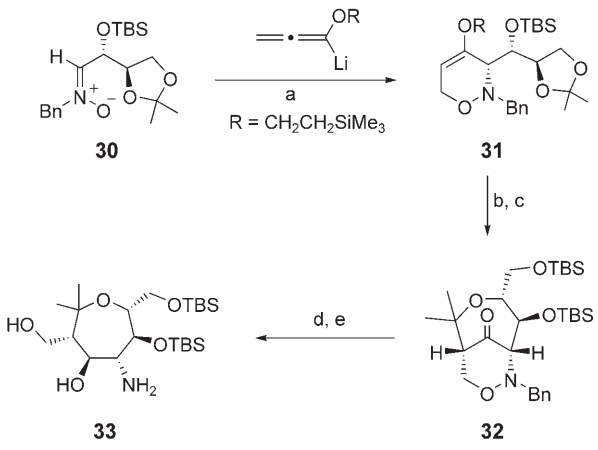
Further stereodefined pyran derivatives synthesized from bicyclic compounds **4** and **6** are presented in Scheme 5.



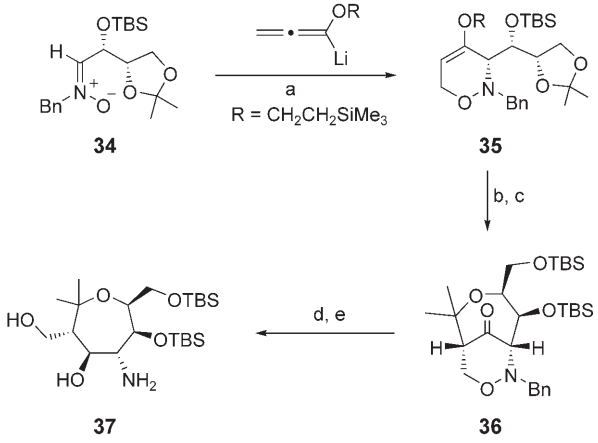
Scheme 5. Reaction conditions: a) MsCl, NEt_3, CH_2Cl_2, 0 °C, 4 h, (quant.); b) $NaBH_4$, EtOH, room temperature, 3 h, (85 %); c) NaN_3, DMF, 90 °C, 6 h, (73 %); d) H_2, Pd/C, MeOH, room temperature, 3 days, (**27**: 81 %); e) $NaBH_4$, EtOH, 0 °C, 4 h, (97 %); f) MsCl, NEt_3, CH_2Cl_2, 0 °C, 4 h, (quant.); g) KSAc, DMF/toluene, 60 °C, 6 h, (**28**: 64 %); h) $Me_3SO^+I^-$, *n*BuLi, −78 °C→RT, 12 h, (**29**: 70 %). Ms = mesyl, DMF = *N*,*N*-dimethylformamide.

Mesylation of the primary hydroxy group of **4**, followed by reduction of the carbonyl group with $NaBH_4$ and introduction of an azido group, generated a new precursor for the reductive ring opening. Hydrogenolysis furnished pyran derivative **27** with an intact azido functionality which may be used for further transformations.[17] Starting from **6**, a thioacetate group can be installed by nucleophilic attack at the corresponding mesylate, resulting in the bicyclic 1,2-oxazine **28** in good overall yield. Treatment with trimethylsulfoxonium iodide stereoselectively transformed **6** into tricyclic compound **29**, which contains an epoxide moiety. Products **27**–**29** and their precursors offer new options for the preparation of highly functionalized enantiopure tetrahydropyran derivatives that can serve as carbohydrate mimetics.

In first experiments we examined whether rings larger than pyrans can be formed by using the rearrangement presented herein. Schemes 6 and 7 show the reaction pathways that led to enantiopure oxepane derivatives in a highly diastereoselective and surprisingly effective manner. The reaction of nitrone **30** (which was easily prepared from D-isoascorbic acid[18]) with lithiated alkoxyallene **1** provided compound **31** with high *syn*/*anti* selectivity. In the presence of $SnCl_4$ in acetonitrile, 1,2-oxazine **31** afforded the desired rearrangement product, which after protection of the primary



Scheme 6. Reaction conditions: a) THF, −78 °C, 2 h, (**31**: 49 %, *syn*/*anti* = 97:3); b) $SnCl_4$ (3 equiv), CH_3CN, −30 °C→RT, 6 h, (76 %); c) *t*$BuMe_2SiOTf$ (3 equiv), NEt_3, CH_2Cl_2, 0 °C, 1 h, (**32**: 92 %); d) $NaBH_4$, EtOH, 0 °C, 4 h, (71 %); e) H_2, Pd/C, MeOH, room temperature, 1 day, (**33**: 82 %).



Scheme 7. Reaction conditions: a) THF, −78 °C, 2 h, (**35**: 71 %, *syn*/*anti* > 97:3); b) $SnCl_4$ (3 equiv), CH_3CN, −30 °C→RT, 6 h, (55 %); c) *t*$BuMe_2SiOTf$ (3 equiv), NEt_3, CH_2Cl_2, 0 °C, 1 h, (**36**: 97 %); d) $NaBH_4$, EtOH, 0 °C, 4 h, (93 %); e) H_2, Pd/C, MeOH, room temperature, 1 day, (**37**: 70 %).

hydroxy group gave bicyclic product **32** in good overall yield. Reduction with $NaBH_4$ followed by hydrogenolysis yielded oxepane derivative **33**, whose constitution and configuration was confirmed by X-ray crystallographic analysis. In the same manner, the stereoisomeric oxepane derivative **37** was prepared from the diastereomeric nitrone **34** (derived from L-ascorbic acid)[18] via intermediates **35** and **36**.[19] Preliminary experiments proved that suitably substituted 1,2-oxazines as precursors opened a route to oxacyclooctane derivatives (oxocanes) in moderate yields.[5]

Our results show that Lewis acid induced rearrangements of 3,6-dihydro-2*H*-1,2-oxazines with 1,3-dioxolanyl substituents and subsequent transformations lead to a variety of polyhydroxylated amino-substituted pyran and oxepane derivatives in an efficient and stereocontrolled manner.[20] The obtained enantiopure oxygen-containing heterocycles can easily be protected selectively (and orthogonally). There-

fore these analogues of aminodesoxy sugars should be of high interest for integration into oligosaccharides.[4,21] Their lipophilicity should be strongly influenced by the nature of alkyl groups R^1 and R^2 (Scheme 2). These compounds also have potential as starting materials for the synthesis of carbohydrate-based β- or γ-amino acids (sugar amino acids) and they can therefore provide novel peptide analogues.[22] The pyran derivatives **6** and **7** can be easily prepared in gram scale and hence they are also candidates for stereodefined scaffolds for the synthesis of polyfunctionalized compounds. This concept has been successfully applied to several carbohydrate derivatives.[23]

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